

VI. *Action of Free Molecules on Radiant Heat, and its Conversion thereby into Sound.**By* JOHN TYNDALL, *F.R.S.*

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§. 1. *Introduction.*

THE experimental researches of RUMFORD and LESLIE raised the subject of Radiant Heat to an extraordinary pitch of interest and importance. Both of these philosophers occupied themselves with what may be called superficial emission and absorption.

MELLONI is to be regarded as the founder of our knowledge of the transmission of radiant heat through solids and liquids. Save in a passing inference, to be noticed immediately, MELLONI left untouched the gaseous form of matter; thinking, probably, that gases and vapours, though their diathermancy could hardly be supposed theoretically perfect, came in this respect so near perfection as to be placed beyond the grasp of laboratory experiment. It was doubtless the general prevalence of this conviction which caused this field of inquiry to lie fallow for so many years after the discovery of the thermo-electric pile.

By an experimental arrangement characteristic of the genius of the man, though, it may be, not quite equal to the requirements of the problem, MELLONI proved that the law of inverse squares held good for radiant heat *in air*, and from this he inferred the absence of all sensible absorption, by air, within the distance embraced by his experi-

\* The substance of this paper was delivered orally as the Bakerian Lecture on November 24, 1881.

ments\*. MELLONI extended to radiation his conclusion regarding absorption. "On ne connaît," he writes, "aucun fait qui démontre directement le pouvoir émissif des fluides élastiques purs et transparents."† Such was MELLONI's relation to the subject now before us.

In 1855 Dr. FRANZ of Berlin published a paper "On the Diathermancy of certain gases and coloured liquids."‡ He found that air contained in tubes 452 and 900 millimeters long, absorbed 3.54 of the radiation from an ARGAND lamp, and he concluded that all transparent gases would behave like air. I have given reasons for holding that Dr. FRANZ in these experiments did not touch the question in hand.§ In the arrangement which he describes, the absorption by air was quite insensible. But 60 per cent. of the radiation from his powerful source was lodged in the glass ends of his tubes; these, as secondary sources, radiated directly and indirectly against his pile, and it was their chilling by the cold air that slightly lowered his deflection and produced the supposed absorption.

It is not improbable that other attempts were made to bring gaseous matter under the dominion of experiment; but none to my knowledge are recorded.

## §. 2. *Partial Summary of previous work.*

My researches on magne-crystallic action carried with them the incessant use of conceptions and reasonings touching molecular constitution and arrangement. At an early period of these studies it occurred to me that heat, both in its radiant and in its ordinary thermometric form, might be turned to good account as an explorer of molecular condition. The first fruit of this idea was a paper "On Molecular Influences,"|| in which it was shown that wood possesses three axes of calorific conduction coincident with the axes of elasticity discovered by SAVART. Experiments on certain crystals recorded in this paper suggested a possible connexion between diathermancy and conductivity, and in 1853 I worked at this question. The substances then submitted to experiment were rock crystal, amethyst, topaz, beryl, rock-salt, smoky quartz, fluor spar, tourmaline, Iceland spar, dichroite, arragonite, heavy spar, flint, and glass of various kinds. These minerals were employed in the shape of cubes carefully cut and polished, the transmission through each of them, in different directions, both of radiant and conducted heat being determined.

A desire for completeness, not then attained, caused me to postpone, and finally to forego the publication of the results of this inquiry. It, however, kept alive reflections

\* "Pour un intervalle de cinq à six mètres, l'air n'exerce aucune absorption sensible pour le rayonnement des corps chauds," 'La Thermo-chrose,' p. 136.

† Annales de Chimie et de Physique, vol. xxii., p. 494.

‡ POGGENDORFF'S Annalen, vol. xciv., p. 337.

§ Philosophical Transactions, 1861, Vol. 151, p. 27, and elsewhere.

|| Ibid., 1853, Vol. 143, p. 217.

on the influence of molecular constitution on the phenomena of radiation and absorption. Encountered continually by the thought that in liquids and solids the pure molecular action was, or might be, hampered by cohesion, the desire to bring, if possible, free molecules under the dominion of experiment beset me more and more.

At the beginning of 1859 I definitely attacked this problem, meeting at the outset difficulties and negations the reverse of encouraging. But after some weeks of labour, I found myself in secure possession of the result that gases and vapours exhibited, in relation to radiant heat, phenomena far more surprising than those observed by MELLONI in liquids and solids. On the 26th of May 1859 the subject was brought before the Royal Society,\* and on the 10th of June I was able, by illuminating the dial of a galvanometer and casting its image upon a screen, to demonstrate in the Royal Institution not only the fact of absorption, but the astonishing differences of absorption which gases and vapours equally transparent to light manifested in regard to radiant heat.†

The following gases and vapours were then examined:—Air, oxygen, hydrogen, nitrogen, carbonic oxide, carbonic acid, nitrous oxide, coal gas, ammonia, olefiant gas, bisulphide of carbon, chloroform, benzol, iodide of ethyl, cyanide of ethyl, formate of ethyl, acetate of ethyl, propionate of ethyl, iodide of amyl, chloride of amyl, amylene, absolute alcohol, amylic alcohol, methylic alcohol, ethylic ether, ethylamylic ether, sulphuric ether, and some others. In the *Philosophical Magazine* for 1862 I have given samples of the results obtained with a few of these substances; and I will here confine myself to the remark that were the measurements there recorded multiplied a hundred-fold, they would fall far short of the number actually executed in 1859.

With a view of compelling the feeblest gases and vapours to show, if they possessed it, their capacity to absorb radiant heat, the “method of compensation” was invented.‡ Without prejudice to the delicacy of the galvanometer, this method enabled me to bring into play quantities of heat far greater than those ever previously invoked, my object being so to exalt the total radiation that a minute fraction of that total should reveal itself to experiment. By this method not only were the feebler gases and vapours coerced, but the vastness of the diathermic range, if I may use the phrase, was established with a clearness and an evidence unattainable by any other means then existent.§

Notices of the investigation having appeared in many English and continental

\* *Proceedings of Royal Society*, vol. x., p. 37.

† *Proceedings of Royal Institution*, vol. iii., p. 155.

‡ *Philosophical Transactions*, 1861, Vol. 151, pp. 6 and 7.

§ With moderate total heats the method of compensation is extremely easy of application; but when the total radiation is very large, some discipline is required to keep the galvanometer needle steady in its most sensitive position. With due training, however, perfect mastery over this difficulty may be obtained.

journals,\* I was induced to defer the detailed publication of the experiments. The investigation itself had taught me the difficulties and dangers which beset it. These had reference both to the methods of experiment and to the purity of the substances employed. To secure the perfect constancy of the sources of heat, and the perfect steadiness of the galvanometer, when the flux of heat was powerful, involved a lengthened discipline. With neither gases nor vapours, moreover, was it easy to obtain uniform results. When generated in different ways, the action of the same gas would sometimes prove itself so discordant as to suggest to me the possible existence of novel allotropic conditions to account for such variations of behaviour. Two samples, moreover, of nominally the same liquid, would furnish vapours yielding results far too divergent to be tolerated. The drying apparatus also contributed its quota of disturbance. These anomalies were finally traced to the fact that an incredibly small amount of impurity derived from the stronger gases or vapours sufficed to disguise and falsify the action of the weaker ones. All this had to be learnt; and when learnt, I thought it desirable, for the sake of accuracy, not to publish the results which had been gained with so much labour, but to go once more, with improved appliances, over the same ground. This I did; though it involved the total abandonment of seven weeks' uninterrupted experimental work in 1859, of seven weeks' similar work in 1860, and of many fragmentary efforts. On the 10th of January, 1861, the memoir containing an account of the investigation was handed in to the Royal Society.†

The first point of importance established in 1859 and developed in the memoir just mentioned was that already referred to; namely, the fact of absorption, and large differences of absorption. The second point—destined, I think, to throw light on the deeper problems of molecular physics—was the proof that while elementary gases offered a scarcely sensible impediment to radiant heat, equally transparent compound gases exhibited, in many cases, an energy of absorption comparable to that of the most athermanous solids and liquids. Determining, for example, the action of a mechanical mixture of two elementary gases, it was proved that without altering either the quantity of matter, or its perfect transparency to light, the absorption of invisible heat might be increased many hundred-fold by the passage of the constituents of the mixture into a state of chemical combination.

\* Proceedings of the Royal Society, May 26, 1859; Proceedings of the Royal Institution, June 10, 1859; Bibliothèque Universelle, July, 1859; Cosmos, vol. 15, p. 321; Nuovo Cimento, vol. 10, p. 196; Comptes Rendus, 1859; and in other journals.

† Section 3 of the Bakerian Lecture for 1861 reveals some of the difficulties which beset the earlier stages of these inquiries. To secure strength of radiation and steadiness of the needle I passed from source to source, obtaining my temperatures in turn from water, oil, fusible metal, sheets of copper heated by regulated flames, and from other things. Approximate results were readily obtainable; but I aimed at a degree of accuracy which would render any material retractation afterwards unnecessary. Soundness of work I thought preferable to rapidity of publication.

A similar deportment may be detected in liquids and solids. The quantity of iodine vapour generated at ordinary temperatures is so small that its action on radiant heat is, as might be expected, insensible. But iodine itself, when liquefied by a powerful solvent, behaves as an almost perfectly transparent body to the obscure calorific rays, even when it is able to extinguish totally the light of the sun. Liquid bromine is also highly diathermanous. The same may be said of phosphorus. In MELLONI'S table, Sicilian sulphur comes next to rocksalt in transmissive power. A concentrated solution of sulphur in bisulphide of carbon exerts no sensible action on radiant heat. By fusing together iodine and sulphur Professor DEWAR has produced a "ray filter" which separates with extreme sharpness the visible from the invisible rays. The remarkable diathermancy of certain specimens of vulcanite, brought to light in the experiments of Mr. GRAHAM BELL and Mr. PREECE, is probably due to the sulphur they contain. MELLONI showed that lampblack is to some extent diathermanous. But when a suitable source of heat is chosen, lampblack proves far more pervious to radiant heat than MELLONI found it to be. An opaque layer of this substance transmits 41 per cent. of the radiation from a hydrogen flame. Were the lampblack optically continuous, the transmission would, doubtless, be still greater. An opaque solution of iodine transmits 99 per cent. of the radiation from the same source, while a layer of pure water 0·07 of an inch in thickness, transmits only 2 per cent. of the radiation from a hydrogen flame. Such results indicate that a profound change in the relation of ponderable matter to the luminiferous ether accompanies the act of chemical combination.

One of my principal aims in the Bakerian Lecture of 1861 was to illustrate the hold which experiment had obtained of a subject previously considered intractable. The densities of the gases and vapours employed were therefore varied within wide limits. In the experimental tube first made use of, a full atmosphere of olefant gas absorbed more than 80 per cent. of the entire radiation, and it was therefore evident that a small fraction of an atmosphere of such a gas would exert a measurable action. On trial, it was found possible to measure the absorption of  $\frac{1}{10,000}$ th of an atmosphere of olefant gas. The action of this gas was determined at sixteen different densities, the absorption, as long as the density was very small, being accurately proportional to the quantity of gas present. Similar experiments were made, and similar results obtained with other gases. The action of sulphuric ether vapour upon radiant heat was proved to be still more powerful than that of olefant gas. The vapour was first carried into the experimental tube by a current of dry air; and the pure vapour was afterwards examined at seventeen different densities. Bisulphide of carbon was tested at twenty different densities; anylene at ten; benzol at twenty; and so of the others.

Considering the views previously entertained regarding the diathermancy of gases and vapours I was naturally impressed with these results. Sceptical when I first observed them, I scrutinised them closely, until repeated scrutiny abolished every

doubt. For my own instruction I illustrated the action of the stronger gases and vapours in a variety of ways. Turning, for example, once rapidly round a cock connecting the exhausted experimental tube with a holder containing a powerful gas, the needle would fly aside, owing to the stoppage of the heat by the infinitesimal amount of gas which entered the tube during the rotation. Discharging a powerful gas or vapour in free air, between the source of heat and the thermopile, a similar energetic action would be produced by the perfectly invisible agent.

I was schooled in such actions before the thought of testing the omnipresent vapour of our atmosphere occurred to me. When it did occur there was in my mind no *à priori* ground for supposing that its action would prove insensible; for why should I assume that  $\frac{1}{100}$ th of an atmosphere of aqueous vapour would prove neutral, after I had proved a small fraction of this fraction, on the part of other gases and vapours, to be active? There was no reason for such an assumption on my part—nothing to deter me from hopefully submitting the question to experiment. I accordingly tested the water vapour of the atmosphere in which I worked, and found its action on a first trial to be thirteen times that of the air in which it was diffused.

It is not uninteresting to compare this approach to the problem with that of a very distinguished man—the late Professor MAGNUS, of Berlin.\* Subsequent to me, he subjected the aqueous vapour of our atmosphere to an experimental test; but he made the experiment under the assured conviction that his result would be negative. “It could,” he says, “be foreseen with certainty that the small amount of aqueous vapour taken up by air at ordinary temperatures could exert no influence on the transmission.” I think it must be obvious that if MAGNUS had gone through the discipline to which I had been subjected, he would not have used this language. His mistake however was a natural one. In fact during the earlier stages of the inquiry my mind was exactly in the condition of his mind—I also thinking, until practically instructed to the contrary, that the action of aqueous vapour at ordinary temperatures must be immeasurably small. It is well known that MAGNUS tested his foregone conclusion, and found it verified; while I, on the other hand, as above stated, justified mine.

The various gases which had been examined in the experimental tube with regard to their powers of absorption, were next tested as regards their powers of radiation. Columns of the heated gases were allowed to ascend in free air, and to radiate against the pile. In this simple way, the radiative power of “transparent elastic fluids” was for the first time established. The order in which the gases ranged themselves, in regard to radiation, was exactly the order of their absorptions. Here, as in other cases, I instructed myself by observing how gases might be made to play the part of solids. Permitting, for example, a film of one of the stronger gases to glide

\* In many respects my generous and helpful friend, but, in regard to this question, my steadfast antagonist for many years.

over a heated surface of polished silver, the radiation from that surface was augmented as it might have been by a coating of isinglass or lampblack.

A surmise has been mentioned regarding new allotropic conditions, as occurring to me amid the perplexities of my earlier experiments. In one instance—that of electrolytic oxygen—the surmise proved correct. My first experiments indicated that the modicum of ozone which went forward with the oxygen, exerted four times the absorption of the gas in which it was diffused.\* Subsequently, by changing the apparatus, and taking pains to augment the quantity of ozone, the multiple rose successively from 4 to 20, 35, 47, 85, ascending finally to 136.† The behaviour of ozone was thus proved to be similar to that of molecules composed of heterogeneous atoms. Hence the conclusion, drawn at the time, that the molecule of ozone was formed of oxygen atoms so grouped as to render their action upon radiant heat virtually that of a compound body. This, it is needless to say, is the constitution now assigned to ozone.

With the view of including corrosive gases and vapours among the number of those examined, and for other reasons, the brass experimental tube was displaced by a tube of glass of the same diameter and nearly 3 feet long. The source of heat was also changed from a LESLIE'S cube, containing boiling water, to a plate of copper against which a sheet of flame was permitted to play. Extraordinary precautions were found necessary to insure perfect steadiness on the part of the flame. With this arrangement the practical inability of the elementary gases to absorb radiant heat was further illustrated and confirmed. Chlorine gas and bromine vapour, for example, were proved to be highly diathermanous.

At the pressure of an atmosphere it was found that the diathermic range of colourless gases extended from 1 to about 1000. The portion of gas first entering the experimental tube, having the whole heat to act upon, produced, as might be expected, the greatest effect, the increment of absorption, after a certain quantity of gas or vapour had entered, being infinitesimal.‡ It was therefore interesting to

\* Philosophical Transactions, Vol. 151, p. 8.

† Ibid., Vol. 152, pp. 84, 85.

‡ This is well illustrated by an experiment on sulphuric ether vapour recorded in the Bakerian Lecture for 1861:—

Pressure.	Absorption.
1 inch	214
2 „	282
3 „	315
4 „	330
5 „	330

The absorption of air being taken as unity, that of sulphuric ether vapour at 1 inch mercury pressure is here shown to be 214. When, however, vapour corresponding to a pressure of 4 inches was already in the experimental tube, the addition of another inch did not sensibly augment the absorption.

compare together the various gases at very small pressures. When the pressure was that of 1 inch of mercury the diathermic range was greatly increased, the absorption by olefiant gas being then at least 6000 times the absorption by atmospheric air.

With the changed apparatus the action of the aqueous vapour of our atmosphere was again taken up, and proved to be, not 13 times, as I had at first supposed, but, on fairly humid days, at least 60 times that of the air in which it was diffused. When, moreover, dried air was caused to pass over moistened glass and then carried into the experimental tube, the absorption was still greater.

A power has been claimed for mist or haze which has been denied to aqueous vapour; but in these experiments concentrated luminous beams, which would have infallibly brought into view the least trace of suspended matter, revealed no mist or dimness of any kind. It is, moreover, demonstrable that an amount of turbidity rendered strikingly evident by a luminous beam, exerts only a fractional part of the action of the pure aqueous vapour. When well dried air was led, not through water or over wet glass, but over bibulous paper, taken apparently dry from the drawers of the laboratory, the amount of vapour carried forward from the pores of the paper produced 72 times the absorption of the air which carried it. After five repetitions of the experiment, wherein the same air was carried over the same paper, a quantity of vapour was still sent forward capable of exerting 47 times the absorption of the air in which it was diffused.

Here the possible action of odours upon radiant heat naturally suggested itself. Many perfumes were accordingly subjected to examination, the odorous substance being in each case carried into the experimental tube by a current of dry air. Thus tested pachouli exerted 30 times, cassia 109 times, while aniseed exerted 372 times the absorption exerted by the air in which it was diffused.

A novel method of exhibiting the absorption and radiation of gaseous bodies, the germ of which had been previously discovered,\* was illustrated and developed by the new apparatus. Suppose the experimental tube exhausted and the needle, under the joint action of the two sources, to be at  $0^{\circ}$ . On admitting a strong vapour the usual deflection would occur. Suppose it to be 50 galvanometric degrees. Let dry air be now introduced until the experimental tube is filled. Although fresh matter is thus thrown athwart the rays of heat, the needle behaves as if the matter within the experimental tube had wholly disappeared. It sinks to zero, and not only so, but passes say to  $50^{\circ}$  on the other side.

After the first moments of perplexity succeeding the observation of this effect, its cause became clear. On entering the experimental tube the air, having its *vis viva* destroyed, was heated dynamically. Incompetent to radiate itself, it imparted its warmth to the vapour, and this powerful radiator poured the heat thus received against the pile. This heat sufficed not only to neutralise the deflection of  $50^{\circ}$  due to

\* Philosophical Transactions, Vol. 151, p. 32.



absorption, and indicating cold, but to carry the needle up to  $50^{\circ}$  on the side of heat. So likewise, when the experimental tube was filled with mixed air and vapour, the needle being at  $0^{\circ}$ , a stroke of the pump, though opening a freer passage for the rays from the source, caused a deflection indicative not of heat, but of cold. Here, the vapour within the tube being chilled by the dilatation of the air, the pile radiated its uncompensated warmth into the vapour and produced the observed deflection.

Such observations suggested a new means of demonstrating the absorption and radiation of heat by gases and vapours. Abandoning all external sources of heat, and permitting the various gases already examined to enter the experimental tube at a common velocity, they became self heated and radiated against the pile. Their radiation, thus determined, corresponded exactly with the results obtained when heated columns of these gases were permitted to rise freely in the atmosphere.

Both the radiation and absorption of vapours were determined in the same manner. The external source of heat was abandoned, and a measured quantity of every vapour was introduced into the experimental tube. Through an orifice of fixed dimensions dry air was then permitted to enter the tube, where the destruction of its *vis viva* raised its temperature. The heated air warmed the vapour, which in its turn radiated the heat imparted to it against the pile. The deflection of the galvanometer declared the strength of this radiation. Absorption was determined by permitting the mixed air and vapour to dilate by a measured quantity, the pile being here the warm body, and the chilled vapour the absorbent. The order in which the vapours stood as regards absorption was here exactly the order of their radiation, while both absorption and radiation, thus determined, agreed with the results obtained by sending the rays from an external source of heat through the pure vapours in the experimental tube.

What has been called "vapour-hesion," whereby liquid films are produced, has been supposed to play a dominant part in my experiments. But it can hardly be imagined that an irregular action of this kind could produce results of such precision and consistency as those here recorded. Such results are, in my opinion, only compatible with the conclusion that the veritable radiators and absorbers are the molecules of the vapours. Apart from all experiment, the notion that vapours must act in this way comes commended to us by the proved, and conceded, deportment of gases. It would be unreasonable to admit that a compound gaseous molecule is active, and at the same time to affirm that a compound vaporous molecule is inert.

This hypothesis of liquid films formed on the interior surface of the experimental tube, and on the plates of rocksalt, becomes, I think, more embarrassed as we proceed. It depends on the unproved assumption that liquids possess powers of absorption which are denied to their vapours. To water and brine, for instance, MAGNUS largely concedes such powers, but not to aqueous vapour. That the state of aggregation exerts an influence is not denied, but that it is here the dominant factor is open to doubt. To admit this would be to concede that the seat of absorption is the molecule

as a whole, to the practical exclusion of the constituent atoms of the molecule. For if the atoms exert any influence, the mere passage from the liquid to the vaporous condition, which separates the molecules from each other, but leaves them individually intact, cannot destroy their powers of absorption.

At an early stage of these researches the parallelism of liquid and vaporous absorption forced itself upon my attention. Thus, my experiments on bisulphide of carbon vapour were connected with the deportment of liquid bisulphide, as set forth in MELLONI'S table. The vapours, moreover, of chloride of sulphur and chloride of phosphorus, whose liquids stand in MELLONI'S table next to bisulphide of carbon, were afterwards proved by me to possess a diathermancy corresponding to that of their liquids. After various references to this subject in preceding memoirs, a portion of the Bakerian Lecture for 1864 was devoted to its examination. Liquid layers enclosed between plates of transparent rocksalt were tested in regard to their diathermancy, and for the sake of control and verification they were employed in five different thicknesses. The vapours of these liquids were examined in quantities proportional to the quantity of liquid, the same quality of heat being applied both to liquids and vapours. By these experiments, it seemed to me placed beyond a doubt, that the liberation of the molecule from the liquid condition did not destroy its absorbent power, the order of absorption being proved to be precisely the same for liquids and their vapours. Ten different substances were shown at the time here referred to to follow this rule. The list has since been extended, and I am not acquainted with a single real exception to the rule. Any reasoning, therefore, which ascribes a potent absorption to perfectly impalpable films, condensed on the surface of my apparatus, and which denies that absorption to the free molecules within the experimental tube, is in my opinion untenable.

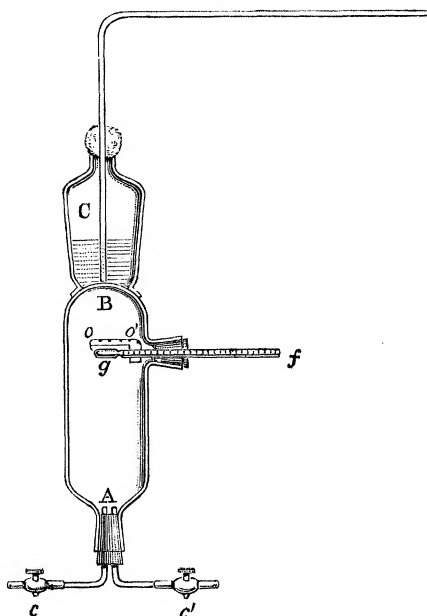
The relation between liquids and their vapours here indicated is very thorough. It extends beyond the field of experiment which we have hitherto had in view. I have, for example, published some researches on the action of rays of high refrangibility on gaseous matter, and have shown in a great variety of cases, that the molecules are shaken asunder by such rays. The actinic clouds, as I have called them, produced by this decomposition, reveal vividly the track of the beam by which they are generated, and render it easy to observe the distance to which the action penetrates. In the case of nitrite of amyl, for example, the power of decomposition is soon exhausted, the actinic cloud ceasing abruptly at a point about 18 inches from the place where the beam enters the vapour. An experimental tube 3 feet long, has therefore one half of its vapour shielded by the other half, and on reversing the tube, the shielded half comes instantly down as an actinic cloud. In the case of iodide of allyl vapour, on the other hand, the beam may pass through a charged experimental tube 5 feet long, fill it with an actinic cloud, and still effect decomposition in another tube placed beyond it. What is true of these vapours is true equally of their liquids; for while a layer of the liquid nitrite  $\frac{1}{8}$ th of an inch thick prevents, when placed in the track of

the beam, the decomposition of its vapour, a layer of the liquid iodide, of quadruple thickness, does not arrest the decomposition. The power, and the lack of power, to penetrate considerable depths is shared alike by the liquids and their vapours. Other, and still more subtle and penetrating illustrations of parallelism between liquid and vaporous absorption are mentioned in the Bakerian Lecture for 1864.\*

### §. 3. *Researches of MAGNUS.*

Prompted by the experiment of GROVE, illustrating the chilling action of hydrogen, MAGNUS, in 1860, began an investigation on the power of gases to *conduct* heat.† His apparatus, traced in outline from his own plate, is shown in fig. 1, where A B is the

Fig. 1.



recipient for the gases, and C a flask containing water kept boiling by a current of steam. The bottom of C, which formed the top of A B, was the source of heat. A thermometer *g f*, shielded by a cork or metal screen *o o* from the radiation of the source, was intended to receive and measure the heat transmitted by conduction. The recipient A B was mounted in a space surrounded by water of a constant temperature. The heating

\* Carbonic acid is one of the feeblest of the compound gases, as regards the radiation from solid bodies; but, for the radiation from a carbonic oxide flame, it transcends all other gases in absorbent power. The action of aqueous vapour is also enhanced when it acts upon the rays emitted by a hydrogen flame. The enhancement extends to water. Curious reversals of diathermic position, when heat from different sources is employed, are moreover shown to occur simultaneously with liquids and vapours.

† A Preliminary Note of this inquiry is published in the "Bericht" of the Berlin Academy for July 30th, 1860. No measurements are given, but certain results are announced. The experiments were first published in POGGENDORFF'S *Annalen* for April, 1861.

of the thermometer, when A B was exhausted,\* was compared with its heating, when A B was filled with various gases, and in every case but one the heating through the gas was found less than the heating through the vacuum. The exception was hydrogen, which carried more heat to the thermometer than was transmitted by the vacuum. The conclusion drawn by its author from this experiment was that hydrogen conducted heat like a metal.

One remark only in this Note has any reference to the diathermancy of gases, but it is a significant one. MAGNUS had no doubt as to the power of every one of his gases to conduct heat. There could, he supposed, be only a difference of degree between them and hydrogen. Whence, then, the lowering of the thermometer? He answers thus:—"From this it is not to be inferred that the gases do not conduct heat, but merely that in their case conduction is so feeble as to be neutralised by adiathermancy." These are the only words in the note which have any reference to radiation.

In his next inquiry, MAGNUS dealt directly with the subject of diathermancy, a Preliminary Note of the investigation being published in the Monatsbericht for February 7th, 1861. This note, like its predecessor, consisted of general and descriptive statements, no actual measurements being given. The completed memoir was first published in POGGENDORFF'S Annalen for April, 1861. For the purposes of this new inquiry the apparatus used in the experiments on gaseous conduction was modified as shown in fig. 2. To the recipient A B a second one G F was attached, both being connected by the tubulure shown in the figure. The recipient G F rested upon the plate of an air-pump, on which also stood the thermopile  $p$ , with one of its faces turned towards the source. From the pile, through the air-pump plate, wires passed to the galvanometer. With this apparatus, the absorption by atmospheric air and by oxygen was found to be 11.12, and by hydrogen 14.1 per cent. of the total radiation. The alleged conductivity of hydrogen did not therefore manifest itself in these experiments.

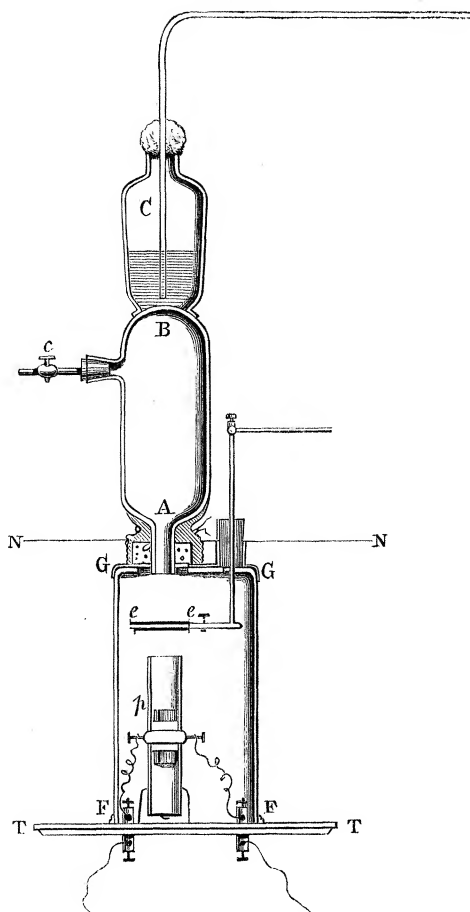
Let us analyse these results. In the first experiments, the distance of the thermometer from the source of heat was 35 millimeters. The action on the thermometer through a vacuum being represented by 100, the action through air and through oxygen of this depth was found to be 82. The loss of 18 per cent. in air and in oxygen was alleged to be due to the adiathermancy of these media, to which percentage, if we wish to ascertain the *total* absorption by air, we should have to add such heat as reached the thermometer by conduction.

Turning now to the modified apparatus, which is evidently drawn to scale, the gas here traversed by the radiant heat was about 275 millimeters in depth, while the stratum traversed in the first experiments was, as stated, only 35 millimeters. Yet in these first experiments an absorption of 18 per cent., while in the later ones an absorption of only 11.21 per cent. is assigned to air. In other words, when the depth of the aerial stratum was augmented more than seven-fold, the absorption, instead of

\* This vacuum temperature, at least in so far as it exceeded that of the sides of the recipient, was obviously derived from the screen.

increasing, fell to less than two-thirds of that of the shallower stratum. It is pretty obvious that an influence different from pure absorption came here into play. That influence was convection.

Fig. 2.



Anxious to probe this matter to the bottom, and to abolish, or account for, the differences between my friend and myself, I wrote to him proposing an exchange of apparatus—that he should send his to London, and I mine to Berlin. I afterwards had a fac-simile of his apparatus constructed in London, and satisfied myself by actual trial that it was really hampered with the defects I had ascribed to it. By means of the striæ of incense smoke and of chloride of ammonium, the fact of convection in air was rendered plainly visible to the eye, while the behaviour of hydrogen, under like circumstances, revealed the cause of its transporting more heat than the vacuum in the first experiments, and less heat, not only than the vacuum, but than air or oxygen, in the second experiments. In the one case, the thermometer, being close to the source, came within the range of the convection currents of this mobile gas, the heat being transported to it by these currents. In the other case, a considerable distance intervened between the source and the pile, which was further effectually protected by the

narrow tubulure. Through it the currents could not pass, but they nevertheless existed in the recipient A B, lowering the temperature of the source without heating the thermoscopic instrument.

The experimental resources of MAGNUS were great, and he here applied them; but the defects of his method were radical and irremovable. These defects reached their culmination in the subsequent researches of Professor BUFF,\* who by pursuing substantially the same method, arrived at the result that a stratum of air  $2\frac{1}{2}$  inches thick absorbed 60 per cent. of the radiation from a source of  $100^{\circ}\text{C}$ .† BUFF also found olefiant gas to be more diathermanous than air, whereas at atmospheric pressures, it is many hundred, and at a pressure of  $\frac{1}{30}$ th of an atmosphere, many thousand times, more opaque to heat.

This is the point at which aqueous vapour enters into the experiments of MAGNUS. When dry and humid air were compared together in his apparatus, no difference between them was observed. But, apart from all disturbance, it would require an instrumental arrangement far more delicate and powerful than that here employed, to bring into view the action of a stratum of mixed air and aqueous vapour 11 inches deep, and having a temperature of only  $15^{\circ}\text{C}$ . Disturbances, however, were not absent. In the first place, the convection currents which enabled dry air to reduce the radiation by 11.12 per cent., were more than sufficient to mask the action of the vapour. Secondly, dry and humid air were brought in succession into direct contact with the face of the thermopile. The pile was therefore affected by any difference of temperature between it and the air, and it could scarcely be supposed that these temperatures were always alike. It was also affected by the condensation and evaporation which occurred when humid air and dry air were brought successively into contact with its lampblack-coated face. To “vapour-hesion” MAGNUS subsequently ascribed very large effects. Here we have the conditions specially suited to the development of the action, and yet no reference is made to it. Either then the disturbance was overlooked, or the apparatus was not sufficiently delicate to reveal it. To these two sources of disturbance—the lowering of the temperature of the source by convection, and the warming and chilling of the pile by contact, condensation, and evaporation—is to be added another, due to the warming which must have occurred when the dynamically heated air came into direct contact with the thermopile—an action which, in my apparatus, proved sufficient to whirl the needle of the galvanometer more than once through an entire circle.

MAGNUS next experimented with glass tubes 1 meter long and closed at the ends with plates of glass. His source of heat was a strong gas flame aided, as in the experiments of Dr. FRANZ, by a parabolic mirror. Two tubes were employed, the one blackened within and the other unblackened. With the blackened tube an absorption

\* Phil. Mag., 5th ser., vol. 4, p. 401. For my reply see Proc. Roy. Soc., vol. 30, p. 10.

† Ibid., 1877, vol. 4, p. 424.

of 2.44 per cent. was found for air, and an absorption of 3.75 per cent. for hydrogen. In the unblackened tube the absorption by air was 14.75 per cent., and by hydrogen 16.27 per cent. of the total radiation.

I went over this ground with the utmost care, using invisible as well as visible heat. But, substituting plates of pellucid rocksalt for the plates of glass, I failed to realise the effect obtained by MAGNUS. He ascribed the difference between the results obtained with his blackened and his unblackened tube to a change of quality in the heat, produced by reflection from the interior surface of the latter. With plates of rocksalt, however, though the reflection abides, the change of quality does not occur. My position, therefore, in regard to these experiments, is similar to what it was in regard to those of Dr. FRANZ. The results obtained with air, oxygen, and hydrogen, were, I hold, due to the chilling of the heated glass ends of the tube by the cold gases, and the consequent lowering of the secondary radiation.

It was shown by MAGNUS himself, and is moreover obvious at first sight, that the unblackened tube sent a far greater amount of heat to the glass plate adjacent to the thermopile than the blackened one. That plate being more heated by the source, was more chilled by the air when it entered. The greater cooling power of hydrogen accounts, moreover, for the advance of the supposed absorption from 14.75 to 16.27 per cent. With carbonic acid MAGNUS detected a difference which had escaped Dr. FRANZ. Instead of making the action of this gas equal to that of air, he found in the blackened tube an absorption of 8.19 per cent., and in the unblackened tube an absorption of 21.92 per cent. exerted by carbonic acid. Here true absorption mixed itself with the effect of mere chilling, while, with still more powerful gases, the effect of chilling retreated by comparison more and more.

Such were the experiments which determined, in the first instance, the attitude of this distinguished man towards that portion of my work which related to the action of the air and vapour of our atmosphere on radiant heat. In the defence of his position he brought to bear all the resources of consummate skill and large experience. His position, however, was by no means a wholly defensive one. He dwelt repeatedly and emphatically on the dangers—and they are real—to which the method pursued by me was exposed. I had closed my experimental tube with plates of transparent rocksalt and he urged against me the hygroscopic character of this substance. Placing rocksalt beside a vessel of water under a glass shade, he found that it could be rendered dripping wet.\* Hence his argument, that, instead of measuring the action of vapour, I had really measured the action of brine. This, however, I could not admit. I was aware of the danger and had avoided it. In many hundred instances the rocksalt plates had been detached from my experimental tube while filled with the very

\* It has been shown by Professor DEWAR that the exposure of a dry plate of rocksalt for 5 minutes to saturated air sensibly augments the weight of the salt as determined by a delicate balance.

air which had produced the observed absorption, and found to be as dry as polished plate glass. For a week at a time I have charged my experimental tube alternately with dried and undried air, removing every evening the plates of salt while the humid air filled the tube. Their dryness and polish were found unimpaired.\* I have frequently flooded the experimental tube with light, and watched narrowly whether any dimness showed itself on the salt, or on the interior surface, when the humid air entered. There was nothing of the kind. I finally abandoned the plates of salt altogether, and obtained in a tube open at both ends substantially the same effects as those obtained when the tube was closed with plates of rocksalt.

In 1862 MAGNUS came to London. He had been previously working at the points of difference between us, and had strengthened his first conviction. The action of the air he had found to be considerable, and the action of aqueous vapour practically nil. I also had been working, but with an entirely different result. It was hoped by both of us that our differences would be settled during this visit. With my closed experimental tube I showed him the neutrality of dry air and the activity of humid air; and while the latter was in the tube I detached the rocksalt plates and placed them in his hand. He closely inspected them, passed his dry handkerchief over them, and frankly and emphatically pronounced them perfectly dry. I then executed in his presence the experiments with the open tube, and reproduced the results which I had previously published. I subjected the method of compensation to a severe test and showed him how exact it could be made. He frankly confessed his inability to find any flaw in my experiments, and save in one particular made no attempt to reconcile our differences. He accounted for the neutrality of dry air observed by me by pointing to my thermopile, between which and the experimental tube a space of air intervened. He argued, and justly argued, that though the calorific rays were permitted to enter the tube from a vacuum, if the air intervening between tube and pile could produce the effect which he ascribed to it, the heat would be robbed of its absorbable rays before the dry air entered the tube, the subsequent neutrality of dry air being a matter of course. The logic was good, but its basis I knew to be more than doubtful; and I therefore asked him whether a layer  $\frac{1}{20}$ th of an inch thick between pile and tube would produce any sensible effect. His reply was an emphatic negative. In subsequent experiments, therefore, the conical reflector was removed from my pile, and placed within the experimental tube, its narrow end being caused to abut against the plate of rocksalt. The face of the pile was then brought within less than  $\frac{1}{20}$ th of an inch of the rocksalt plate; and in this way my former measurements, which had declared the pure air of our atmosphere to be a practical vacuum to radiant heat, were verified to the letter.

The well-earned fame of MAGNUS as an experimenter, and his personal friendliness to myself, rendered it specially incumbent on me to deal respectfully with every one of his suggestions. He once intimated to me that the absorption which I had supposed

\* This mastery over the apparatus was not attained without training. Any lapse of care soon declared itself by the condition of the plates of salt.



due to aqueous vapour, might be really due to the smoke and dust suspended in London air. To meet this I carried air myself from the Isle of Wight, had it carried from Epsom Downs and other places, and found the aqueous vapour diffused in such air to be from 60 to 70 times more energetic than the air itself. London air, moreover, was freed from its suspended matter and tested when dry: it proved neutral. The self same air was then rendered humid: its absorbent power was restored. Then, with dry air as a carrier, I introduced smoke into the experimental tube, until it far exceeded in density that suspended in the London air when MAGNUS drew my attention to it. The quantity of heat intercepted by this smoke proved to be only a fraction of that absorbed by the perfectly invisible aqueous vapour.

On his return to Berlin he resumed his labours. He had been especially impressed by the experiments with the open tube, and to this point he directed his chief attention. "The result of this experiment," he writes, "was so surprising and so little in accord with what I had found by other methods, that on reaching home I determined to repeat the experiment." He did so, with this result:—"I have," he says, "repeated the blowing in of dry air and moist air many hundred times; but in no single case was the deflection such as to indicate a greater absorption by moist air."\* Humid air in his experiments produced the deflection of heat; dry air the deflection of cold—a result diametrically opposed to mine. In London he had seen that my deflections were as large as I had affirmed them to be, but he had not criticised them with a view of ascertaining whether they were or were not in the right direction. In these new experiments, however, he had, he thought, hit upon their origin. The moving air had reached the face of the thermopile, producing, when humid, heat by condensation, and when dry, cold by evaporation.

I read the account of these experiments with some concern; for it was thereby made plain to me that MAGNUS had by no means realised the anxious care that I had bestowed upon my work. The testimony of an independent observer would, I thought, set the matter right. My apparatus, carefully adjusted, was accordingly handed over to Dr. FRANKLAND, who minutely tested every point involved in, or arising out of, the objection of MAGNUS. He verified all my results. His opinion as to the accuracy of the method of compensation is worth recording. "In conclusion," he writes, "I cannot but express my surprise and admiration at the precision and sharpness of the indications of your apparatus. Without having actually worked with it I should not have thought it possible to obtain these qualities in so high a degree in determinations of such extreme delicacy."† To this may be added the subsequent testimony of Professor

\* POGGENDORFF'S *Annalen*, 1863, vol. 118, p. 580; *Phil. Mag.*, 1863, vol. 26, p. 25.

† The total heat here employed amounted to  $86.2^\circ$  of a quadrant. This exceedingly large deflection was neutralised by the radiation from the compensating cube. But so accurately were the two sources balanced, and so constant was the radiation on both sides, that the determinations were made with ease, and without sensible disturbance or fluctuation.

WILD, now of the University of St. Petersburg, who went carefully over the same ground. "In all my experiments," he says, "conducted according to TYNDALL'S method, which included more than a hundred distinct observations, I have never obtained deflections of the galvanometer needle in contradiction to the statements of Professor TYNDALL."\*

In an extremely able paper, a translation of which is published in the *Philosophical Magazine* for October, 1866, the Petersburg philosopher compares the methods pursued by MAGNUS and myself respectively. Insufficient sensitiveness and the disturbance due to convection currents, caused him, he says, to abandon the method of MAGNUS. "Although," he continues, "this method of investigating absorption may, in the hands of so experienced and expert an experimenter as Professor MAGNUS, be an appropriate one for determining absolute values with great certainty, I feel bound, from my own experience, to give a decided preference to TYNDALL'S method, not only on account of the greater facility with which it furnishes qualitative [quantitative] results, but also in consequence of its greater delicacy. It is principally in consequence of this greater delicacy that, notwithstanding the negative results furnished by MAGNUS'S method, I maintain that the greater absorptive power of moist air, as compared with dry, has been fully established by the experiments made according to TYNDALL'S method; and I am of opinion that meteorologists may without hesitation accept this new fact in their endeavours to explain phenomena which hitherto have remained more or less enigmatical."

In 1866 MAGNUS varied his method of experiment, seeking to solve the question of absorption by observations on radiation. "I have," he says, "made a few determinations of the radiation of dry and moist air, and of some other gases and vapours. Up to the present time," he continues, "the capacity of these bodies to transmit heat has alone been determined."† He then describes his arrangement:—"The gases and vapours were passed through a brass tube of 15 millimeters internal diameter, which was placed horizontally and heated by gas flames. One end of the tube was bent upwards so that the heated air ascended vertically, while at a distance of 400 millimeters from the vertical current, was placed the thermopile." When dry air was sent through this tube, the deflection produced was three divisions of a scale; when air which had passed through water at a temperature of 15° C. was sent through the tube, the deflection rose to five divisions; when the water was warmed to 60° or 80° FAHR., the deflection was 20 divisions; and when the water boiled, the deflection was 100 divisions. In this last experiment, however, a mist appeared, so that, as urged at the time, the radiation could not be said to have been purely from vapour. In the other cases no mist was visible, but it was nevertheless concluded that the 20-division deflection was due to the formation of mist at the boundary of the ascending current.

\* *Phil. Mag.*, 4th ser., vol. 32, p. 252.

† This is an inadvertence. Exhaustive experiments on the radiation of gases and vapours had been made and published many years previously.

I should be disposed to claim these experiments as telling in my favour. The first of them, in my opinion, dealt with the radiation not from dry air but from the adjacent aqueous vapour which had been warmed by the dry air. That the deflection in the second experiment was small is not surprising. The radiation which could reach the pile from a jet of air only 15 millimeters in diameter, and containing such moisture as could be taken up at  $15^{\circ}\text{C}$ ., must have been extremely small under any circumstances. But in the present case, even this small radiation was diminished by the passage of the heat through 400 millimeters of undried air. I should demur to the explanation of the third experiment, and question the warrant to imagine a mist which could not be seen. Even the fourth experiment, where mist was visible, yielded, I doubt not, a mixed result; part of the effect, and probably the smallest part, being due to the mist, and part of it to the vapour.

With regard to the radiation from hot aqueous vapour, the following experiment is typical of some hundreds which I have had occasion to make. A burner consisting of two rings provided with numerous small apertures was placed within a square tin chimney. At some height above the burner the chimney was perforated so as to enable the radiation from a heated gaseous column within the chimney to reach a distant thermopile. The side of the chimney facing the pile was so protected by screens that the radiation from the chimney itself was nil. Connecting the burner with a bottle of compressed hydrogen the gas was ignited. A column of hot vapour rose from the burner and passed the aperture in the chimney, through which it sent its rays to the pile. Mere tips of flame were first employed; the column of vapour rising from them sufficed nevertheless to produce a permanent deflection of

$40^{\circ}$

A slight augmentation of the flame sent the needle up to

$60^{\circ}$

A still further augmentation sent it up to

$75^{\circ}$

This last deflection was equivalent to more than 400 of the degrees in the neighbourhood of zero.

The radiating column was here considerably above the flame. To examine the condition of the column a concentrated luminous beam was directed upon it. There was no precipitation. On the contrary, the suspended matter in the air of the chimney was much less than that of the surrounding air. Instead of a white mist, we had the blackness due to the destruction of the floating matter by the hydrogen flame.

On quenching the flame the needle returned accurately to zero.

In his objections MAGNUS, for the most part, dealt with true causes, but he erred as to their scope of action. I never denied the existence of the dangers which he emphasized. The hygroscopic character of rocksalt, for example, to which he recurred so often, cannot be questioned. It has a strong attraction for moisture, especially when cold. On this point my experience has been large, and I applied it in the execution

of my experiments. These, as I have so frequently stated, were conducted with plates of salt as dry as polished glass or rock crystal. Thus, while conceding the fact that rocksalt is hygroscopic, I demur to its application.

A similar remark applies to the last solution offered by MAGNUS of the differences between us. In 1867, he showed that vapours were condensed by surface attraction to a greater extent than had previously been supposed. Blowing vapour-laden air into a metal tube, he found that heat was generated. He inferred, and rightly inferred, that this heat was produced by the condensation which occurred on the interior surface. This condensation he found to depend on the condition of the surface, being greater when it was tarnished or coated than when it was polished. He saturated air with moisture at a temperature of  $16^{\circ}$  C., and then raised both it and his pile to a temperature of  $38^{\circ}$ . When such air was blown against the dry face of the pile heat was generated. Condensation therefore occurred upon a surface  $22^{\circ}$  C. higher than the dew point of the vapour. Against this I have nothing to urge. But the fact by no means justifies the inference drawn from it, which was, that the vapours in my experimental tube were converted by "vapour-hesion" into liquid layers of high opacity to radiant heat. These layers, acting upon the calorific rays impinging on the interior surface of my tube, produced the absorption which I had erroneously ascribed to the vapours. More than this, the liquid layers were supposed to be broken up into discontinuous patches which not only absorbed the heat but scattered it. "Vapour-hesion," it may be added, was found to vary with the liquid which produced the vapour, being particularly strong in the case of alcohol.

MAGNUS brought this generalization to the test of experiment, but failed to verify it. He urged humid air against a dry mirror, from which radiant heat was reflected; but unless he wetted the mirror visibly no effect was produced on the reflected beam. Still he held that reflection, oft repeated, rendered sensible an action which eluded a single reflection. My position here is clear. I do not doubt surface attraction, or deny the existence of impalpable films. No experiment was ever made on the reflection of light or radiant heat in which such films did not intervene, but they had as little effect upon my results as they had upon those of DE LA PROVOSTAYE and DESAINS,\* and of other refined experimenters. As early as 1859, I was made aware of the danger which might arise from condensation. Warned by the action of chlorine on my brass experimental tube, I coated it inside with lampblack, and re-tested with it all my vapours. The result removed from my mind the suspicion that surface condensation had anything to do with the observed absorption. Many similar experiments with blackened tubes were subsequently made by me for my own safety and instruction. There was no substantial difference between the results obtained

\* Considering the energy of water as a radiator, exceeding according to LESLIE that of lampblack itself, the film of this liquid which must have covered the plates of silver in the experiments of the two French philosophers ought, if MAGNUS be correct, to have sensibly raised the emission. Calling the emission from lampblack 100, that from polished silver plus the film was only 2.1.

with such tubes, and those obtained with polished tubes in which internal reflection came into play.

Such are the general features and phases of a discussion which, though dealing only with a small item of my work, has consumed a considerable amount of time. Other able experimenters have entered this field, the latest of whom, MM. LECHER and PERENTER, have published a long and learned memoir in WIEDEMANN'S *Annalen*, which has been translated in the *Philosophical Magazine* for January, 1881. My experiments with gases they corroborate, but not those with vapours. Regarding the action of aqueous vapour they are especially emphatic, their conclusion being: "that moist air does not perceptibly absorb the heat rays from a source of  $100^{\circ}$  C." In fact they found moist air a little more transparent than a vacuum. "No imaginable source of error," they affirm, "has here been left out of account." The arrangement for filling with moist air was varied, the air allowed to stand for a long time over the water in the gas-holder, and this moist air then passed through several wash-bottles into the experimental space, but with the same *negative* result." In common with MAGNUS, MM. LECHER and PERENTER ascribe my results to the condensation of liquid films on the rocksalt plates, and on the polished inner surface of my tube.\*

#### §. 4. *Experiments resumed: Verifications.*

With a view to my own instruction, and to the removal of uncertainty from other minds, these researches on radiant heat were resumed in November, 1880. A brass experimental tube 4 feet long,  $2\frac{3}{8}$ th inches in diameter, and polished within, was first employed.† Interposed between it and the source was a "front chamber" through which, when exhausted, the rays passed into the experimental tube. A plate of transparent rocksalt separated the tube from the chamber; while a second plate of salt closed the distant end of the experimental tube. The source of heat was at first a LESLIE'S cube containing water at  $100^{\circ}$  C., to one of the faces of which the end of the front chamber was carefully soldered. The chamber also passed air-tight through a copper cell in which a continuous circulation of cold water was kept up. The heat which might otherwise have reached the experimental tube by conduction from the source was thus cut off. One face of a thermopile, provided with

\* However I may otherwise differ from MM. LECHER and PERENTER, I agree with their opening remark, that few other questions of experimental physics present difficulties so great as the one here under consideration. Nor do I see reason to differ from their closing words, that "the extraordinary difficulty of investigations of this sort would be richly repaid by the attainment of quantitative results; whilst the corresponding optical investigations (immeasurably easier) will always remain more of a qualitative nature." It is the difficulty here signalled that has caused so many distinguished investigators to go astray in this field of inquiry. I may state here that on the receipt of their paper I wrote to MM. LECHER and PERENTER, but my communication was returned from Vienna through the dead letter office.

† The plate answering to this description will be found in the *Philosophical Transactions* for 1861.

a reflecting cone, received the rays which passed through the experimental tube. The other face, also provided with a cone, received the rays from a "compensating cube," used, as formerly, to neutralise the radiation from the source, and to bring the needle of the galvanometer to zero when the experimental tube was exhausted. On the entrance then of any absorbent gas or vapour the equilibrium was destroyed, the needle moved from zero, and from the observed permanent deflection the absorption was calculated. Other qualities of heat, and other experimental tubes than that here described, were afterwards introduced into the inquiry.

I here give the measurements executed in 1880 with the vapours of nine different liquids, in experimental tubes of the dimensions above given.

TABLE I.

	Pressures.	Vapours.		Liquids. Red hot spiral.
		LESLIE'S cube vacuum.	LESLIE'S cube free.	
Bisulphide of Carbon . . . . .	·48 in. mer.	4·4	5·0	7·6
Chloroform . . . . .	·36 „	12·8	12·9	28·8
Benzol . . . . .	·32 „	14·8	15·0	44·5
Iodide of Ethyl . . . . .	·36 „	18·4	19·3	47·0
Iodide of Methyl . . . . .	·46 „	25·0	26·2	59·0
Amylene . . . . .	·26 „	26·1	27·2	65·0
Sulphuric Ether . . . . .	·28 „	35·0	35·6	71·0
Acetic Ether . . . . .	·29 „	43·3	43·7	77·5
Formic Ether . . . . .	·36 „	43·3	44·0	78·0

The "pressures" in this table are chosen with a view to the comparison of liquids and vapours. They express quantities of vapour which are proportional to the quantities of matter in the respective liquids at a common thickness. The two next columns contain the absorptions per 100, of the heat from two LESLIE'S cubes, the one with a vacuum in front of it, the other placed in free air, and well protected from air-currents. The close agreement of the two columns proves the "front chamber" to be a superfluity. It also illustrates the coincidence to be attained in these measurements when they are carefully made. In the last column I have placed the absorptions exerted by liquid layers of the respective substances at a common thickness of one millimeter. The source of heat here was an incandescent platinum spiral. The order of absorption of liquids and vapours is the same.

This order is, as might be expected, undisturbed, when we apply heat of the same quality to liquids and vapours respectively. This is shown by the following table :—

TABLE II.

	Polished tube.		Blackened tube.
	Spiral (dull).	Spiral (bright).	Spiral (dull).
Bisulphide of Carbon . . . . .	3·0	2·4	3·0
Chloroform . . . . .	7·0	4·6	5·0
Benzol . . . . .	9·4	7·5	10·0
Iodide of Ethyl . . . . .	13·6	8·6	12·3
Iodide of Methyl. . . . .	15·6	10·7	13·8
Amylene . . . . .	20·6	14·3	17·5
Sulphuric Ether. . . . .	27·0	21·0	23·8
Acetic Ether . . . . .	33·0	23·0	29·0
Formic Ether. . . . .	33·0	23·0	30·0

The vapour pressures here are the same as those employed in Table I. The order of absorption is the same in both tables; but its amount is diminished. This was to be expected from the difference in quality of the heat. We are dealing with transparent vapours—in other words, vapours pervious to the luminous rays; and the greater the proportion of these rays in the calorific beam, the less will be the absorption. This is well illustrated by the second column in the table, which shows the fall of the absorption when the spiral is raised from a dull red to almost a white heat. The polished tube was used in both these cases.

The third column of figures in Table II. shows the results obtained when the experimental tube was coated within with lampblack. The absorptions are in the same order, and almost of the same amount as those of the first column. The case is representative and might be multiplied to any extent. It is incompatible with the notion that my results were due to films collected on the polished interior surface of my experimental tube.

Placing the substances recently experimented on in the order of their absorption, and also in the order which they exhibited in 1864, we have the following two columns:—

1880.	1864.
Bisulphide of Carbon	Bisulphide of Carbon
Chloroform	Chloroform
Benzol	Iodide of Methyl
Iodide of Ethyl	Iodide of Ethyl
Iodide of Methyl	Benzol
Amylene	Amylene
Sulphuric Ether	Sulphuric Ether
Acetic Ether	Acetic Ether
Formic Ether	Formic Ether

In 1864, therefore, the iodide of methyl proved itself more diathermanous than the

iodide of ethyl, while both of them were more diathermanous than benzol. In 1880, the case was precisely the reverse. Suspecting that the discrepancy might be due to impurity, I requested my friend Professor DEWAR to subject the liquids to a further process of purification. Tested afterwards, they produced the following deflections :—

	A	B	C
Bisulphide of Carbon . . . . .	5.0°	5.0°	4.0°
Chloroform . . . . .	17.0	15.0	6.0
Iodide of Methyl . . . . .	39.4	33.0	8.0
Iodide of Ethyl . . . . .	33.0	35.0	12.5
Amylene . . . . .	42.0	41.0	16.0
Sulphuric Ether . . . . .	44.3	43.5	18.2
Acetic Ether . . . . .	46.2	45.5	22.0
Formic Ether . . . . .	47.5	46.9	22.2

Under A and B respectively are the deflections produced by the liquids prior to and after purification. The iodide of methyl falls from 39.4° to 33°, while the iodide of ethyl rises from 33° to 35°. The relative positions occupied by the liquids in 1864 are thus restored. Benzol, however, remained permanently lower than before. Under C are the deflections produced by the vapours of the purified liquids. Here also the positions of the two iodides are reversed, vaporous absorption following the order of liquid absorption. I have frequently encountered cases of this character. The simultaneous change of diathermic position of liquid and vapour indicates that the foreign ingredient, whatever it was, possessed approximately the same volatility as the substance which it vitiated.

## §. 5. *New Experiments. Hypothesis of Internal Films.*

### *a. The Experimental Tube.*

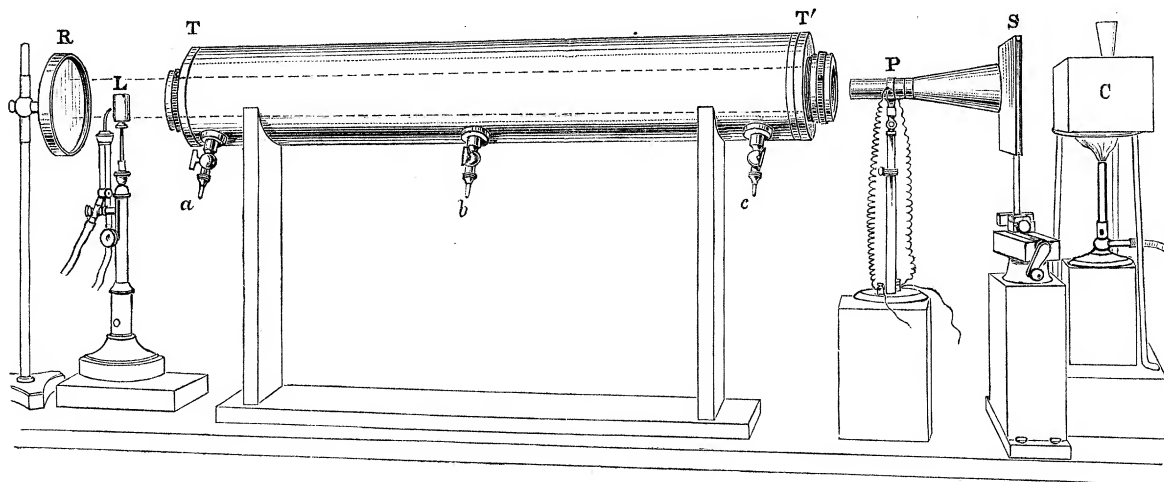
I wish now to come to closer quarters with the argument urged by MAGNUS and repeated by MM. LECHER and PERNTER, namely that my results were due to “vapour-hesion”—that is to say to liquid films condensed on my experimental tube and on my plates of rocksalt. The two investigators last named express unqualified surprise that I should have neglected the simple precaution of experimenting with blackened tubes. But this precaution was by no means neglected by me. I have repeatedly fortified myself by experiments of this character, with the result recorded in Table I. But I went further. A smooth coating of lampblack, however powerful as an absorber, might be held competent to reflect a certain portion of the incident heat. Hence my desire to get entirely rid of reflection, by avoiding all contact with the interior surface of the experimental tube.

In fig. 3 an apparatus is sketched by means of which this has been accomplished. T T' is a stout tube of brass, 36 inches long and of 6 inches internal diameter. Projecting from its otherwise closed ends are screws 1 inch each in depth, surrounding



circular apertures  $3\frac{1}{8}$  inches in diameter. By means of screw caps these apertures may be closed air-tight by transparent plates of rocksalt, the plates being protected from crushing by washers of indiarubber. *a* is a cock leading to an air-pump and a barometer tube, *b* is a cock to which flasks can be attached, while *c* is a cock connected with a purifying apparatus (not shown). This consists of a U tube filled with fragments of clean glass moistened with sulphuric acid, and of a second tube filled with fragments of Carrara marble wetted with caustic potash. A plug of cotton wool intercepts the floating matter of the air. The source of heat *L* is a cylinder of carefully prepared lime, against which a flame of coal gas and oxygen impinges. The incandescent lime faces the concave mirror *R*, which receives the rays and sends them back in a parallel beam through the tube *T T'*. *P* is the thermopile from which wires proceed to a distant galvanometer, the reflected dial of which is observed through a telescope. *S* is an adjusting screen. At *C* is what, in my former researches, I have called the "compensating cube," used to neutralise the radiation from the source *L*, and to bring the galvanometer needle to zero. The chief object of this arrangement is to enable the experimenter to send a calorific beam along the axis of the tube *T T'*, which shall never touch its internal surface. The great width of the tube, aided when necessary by diaphragms, renders this easy of accomplishment.

Fig. 3.

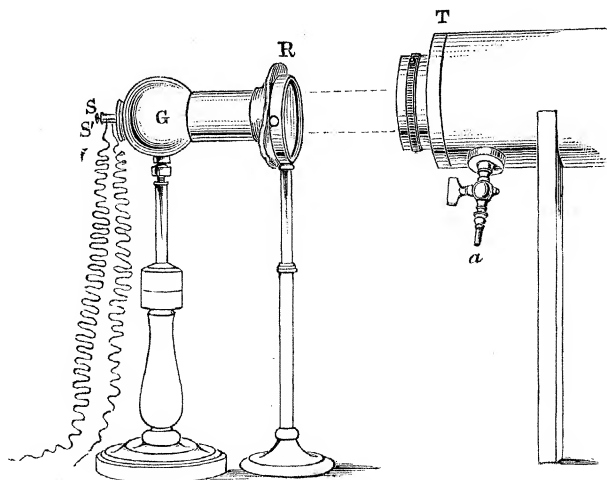


The mode of operation is readily understood. Suppose the heat impinging on the pile to produce a galvanometric deflection of  $50^\circ$ . This, the "total heat," is neutralised by the radiation from the compensating cube. To render the compensation accurate, the double screen *S* is shifted by an extremely fine screw motion. Even when the total heat is very large it is possible, by means of this screen, to neutralise accurately the radiation of the source and bring the needle to zero. Suppose it to be there when the tube *T T'* is exhausted; on permitting a gas or vapour capable of absorbing

radiant heat to enter T T', the pre-existing equilibrium is destroyed; the needle moves promptly away from zero, and from the observed deflection the absorption may be calculated.

Instead of the concave reflector, a rocksalt lens of great purity is sometimes used to render the beam parallel. When the lens is used, the incandescent portion of the cylinder of lime is caused to face the tube T T', between which and the lime the lens is introduced. Instead of the incandescent lime, a spiral of platinum wire heated to redness by a voltaic current is frequently employed as the source of heat. The spiral is placed in the centre of a brass globe G, fig. 4, and is connected with the screws S S'

Fig. 4.



fixed in the back of the globe, from which wires pass to the battery. R shows the position of the rocksalt lens, while one end of the experimental tube is shown at T. The greatest care is here necessary to protect the spiral from any agitation of the air. Such care, however, it is always in the experimenter's power to bestow. To secure constancy in the radiation, the battery was charged three times a day, the strength of the current being regulated by a rheostat, and checked by a tangent galvanometer.

An experimental tube of the description shown in fig. 3 was first employed by me about twelve years ago, and with it I then verified all the experiments I had previously made on the absorption of radiant heat by gases and vapours. The experiments were not published in any scientific journal, but they are thus referred to at page 394 of my volume of collected memoirs, entitled "Contributions to Molecular Physics in the domain of Radiant Heat":—"The two ends of an experimental tube 38 inches long and 6 inches in diameter were each provided with an aperture 2·6 inches in diameter. These apertures were closed with plates of rocksalt. The source of heat was a platinum spiral, well defended from air-currents, and heated to redness by an electric current. In front of the spiral was a rocksalt lens, which sent a slightly convergent beam through the tube. Behind the most distant plate was formed a sharply defined

image of the spiral, its size being such *that it was wholly embraced by the plate of salt*. Here then was a beam of heat passing through an experimental tube without coming into contact either with the surface of the tube itself, or with any coating or lining of that surface. With this apparatus all my old experiments on vapours have been frequently repeated. There is no substantial difference between the results thus obtained, and those obtained with an experimental tube, where nineteen-twentieths of the heat which reached the pile, was reflected heat."

The tube referred to in this extract was of rough brass, tarnished within. Hence, when air entered it, after exhaustion, the dynamic heating of the tube and the partial condensation of the vapour when the air was moist, produced an amount of radiation from its internal surface which, though small, was a source of some disturbance. In my present experiments, therefore, another tube of the dimensions above given is employed, and to reduce to a minimum any radiation from its internal surface, it is coated within with silver, deposited electrolytically and highly polished. Experiments with this tube show that it does not in any way disturb the true radiation from the source.

In Table I. are recorded five series of measurements executed with a brass tube polished within. But as the liquids, though reported pure by the manufacturing chemist, vary slightly from time to time, I thought it advisable to adhere to the same samples in experiments wherein a tube with reflecting interior is to be compared with one permitting of no reflection. The following five series of new measurements were therefore executed with the tube first mentioned.

TABLE III.

BRASS tube with internal reflection.

	Pressures.	A Spiral (dark).	B Spiral (bright).	C Lime (free).	D Lime (mirror).	E Lime (lens).
Bisulphide of Carbon . . . . .	·48	5·0	3·1	3·4	3·1	2·5
Chloroform. . . . .	·36	7·9	5·3	5·6	4·8	5·0
Benzol . . . . .	·32	9·6	8·6	7·9	6·9	6·3
Iodide of Methyl . . . . .	·46	12·1	8·8	10·2	8·1	7·5
Iodide of Ethyl . . . . .	·36	15·0	11·9	12·5	11·3	10·6
Amylene . . . . .	·26	21·9	15·6	16·0	14·4	12·5
Sulphuric Ether . . . . .	·28	30·9	23·1	22·7	19·8	18·1
Acetic Ether . . . . .	·29	36·9	27·3	29·6	24·1	..
Formic Ether. . . . .	·36	..	..	29·6	25·0	23·8

Column A in this table contains the absorptions of the respective vapours, in hundredths of the total radiation, when the source was a platinum spiral just under incandescence, unaided by either lens or mirror. Under B are the absorptions when the source was the same spiral heated to bright redness. The same vibrating atoms are preserved, but in A they vibrate on the whole more slowly than in B; and as

the atomic periods of the transparent vapours synchronise best with the slower oscillations, the absorptions in A are considerably higher than those in B. Under C are the absorptions when the source was a moderate limelight, produced by coal gas and oxygen. Under D are the absorptions when the source was the limelight, with its heat gathered up and sent through the experimental tube by a concave mirror, while under E are the absorptions of the heat of the incandescent spiral aided by a rocksalt lens. The absorptions in D and E are somewhat less than those in C, because the path of the rays was diminished, through the reduction of internal reflection by the mirror and lens.

With the foregoing results, obtained with the brass experimental tube polished within, where the greater portion of the heat reaching the pile had undergone reflection, are now to be compared those obtained with the silvered tube, where internal reflection was wholly avoided.

TABLE IV.

WIDE silvered tube with no reflection.

	L A Spiral (dark).	L B Spiral (bright).	M C Lime (bright).	M D Lime (moderate).	L E Lime (dull red).
Bisulphide of Carbon . . . . .	4.0	1.8	1.5	1.5	3.3
Chloroform . . . . .	5.6	3.0	3.5	4.2	6.0
Benzol . . . . .	7.0	5.1	4.4	6.3	8.0
Iodide of Methyl . . . . .	7.5	5.9	5.0	6.5	9.2
Iodide of Ethyl . . . . .	11.3	7.6	6.8	8.5	11.2
Amylene . . . . .	15.0	11.8	8.8	12.0	17.3
Sulphuric Ether. . . . .	21.2	17.1	12.5	15.0	25.0
Acetic Ether . . . . .	26.0	20.0	16.3	24.0	32.0
Formic Ether . . . . .	27.0	21.0	17.0	25.0	34.0

The vapour pressures here were those given in Table III. Column A contains the absorptions measured when the source of heat was a spiral under incandescence, aided by a rocksalt lens. B contains the absorptions measured with the same arrangement, the spiral being raised to bright redness. As usual the heat of lowest refrangibility is most absorbed. C contains the absorptions of a tolerably intense limelight aided by the silvered mirror. D the absorptions of the same light with its intensity reduced, while E contains the absorptions of the rays from a lime cylinder heated to dull redness by a steady flame of hydrogen, burning in air, and aided by a rocksalt lens.

Here, then, where no trace of reflected heat is sent to the pile, we have substantially the same results as those obtained when by far the greater portion of the heat reaching the pile had undergone reflection. The agreement shows that the films, the action of which had been posited, but never proved, are, in regard to this action, what I always knew them to be, imaginary.

*b. The Plates of Rocksalt.*

Having thus, I trust effectually, disposed of the hypothesis which ascribed my results to liquid layers covering the interior surface of the experimental tube, I proceed to the examination of the plates of rocksalt which have also been credited with a liquid deposit. This hypothesis is to a great extent disposed of in a paper of mine published in the Philosophical Transactions for 1864; which, like other papers, has been overlooked by writers on this question. An apparatus is there described which enabled me to operate upon gaseous strata of different thicknesses, the thickness, in each case, being measured with great accuracy by aid of a vernier. Let two polished plates of rocksalt be supposed in close contact with each other, and let them be gradually separated by a suitable rack-and-pinion movement. From the first moment of their separation let the space between them be copiously supplied with vapour. Liquid films, if they form at all, will be deposited when the distance between the plates of salt is but small. As far as the films are concerned, they will be as influential when the plates are  $\frac{1}{20}$ th of an inch apart as when they are 2 inches apart. Hence, if the hypothesis of my opponents be correct, the absorption ought to declare itself with the former amount of separation as clearly as with the latter. But if, as I allege, the absorption be the act of the vapour molecules, then the deepening of the vapour stratum will be accompanied by an increase of the absorption. The following experiment bearing directly on this subject was executed in 1864. My plates of salt were first fixed at a distance of  $\frac{1}{20}$ th of an inch asunder, and the space between them was copiously supplied with air saturated with sulphuric ether vapour. The distance between the plates of salt was then augmented by steps, as shown in the following table, and at each step the absorption was determined. Here are the results:—

Thickness of vapour stratum.	Absorption.
0·05 inch . . . . .	2·1 per cent.
0·1     „ . . . . .	4·6     „
0·2     „ . . . . .	8·7     „
0·4     „ . . . . .	14·3    „
0·8     „ . . . . .	21·0    „
1·5     „ . . . . .	34·6    „
2·0     „ . . . . .	35·1    „

We thus see that when the depth of the vapour stratum augments from  $\frac{1}{20}$ th of an inch to 2 inches, the absorption augments from 2 per cent. to 35 per cent. of the total radiation.

It is only with sulphuric ether that an absorption of 2 per cent. by the thinnest stratum could be obtained. With most other vapours the action of a layer  $\frac{1}{20}$ th of an inch in thickness proved insensible. We may thus begin with a layer which yields an

absorption immeasurably small, gradually augment the thickness of the absorbing layer until it becomes a column 38 inches long, and find, throughout, the increase of absorption running hand in hand with the increase of the length of the absorbent layer. This result is utterly irreconcilable with the hypothesis that liquid layers on the plates of salt played any important part in my experiments.

With regard to "vapour-hesion," I have to make the following further remarks. Let a thin plate of polished rocksalt be placed upon, or against, the face of the thermopile, with its lampblack removed, so as to expose a clean metallic surface. Let an open glass tube end about a quarter of an inch above the plate of salt; and through this tube let a current of mixed air and vapour be gently urged downwards against the plate. No fine spray, which might readily arise from bubbling through a liquid, is to be permitted to mingle with the vapour. My vapours, I may say, have been usually formed, without bubbling, in large flasks, each containing a portion of a volatile liquid, the vapour of which was permitted to diffuse in the air of the flask. FLETCHER's foot-bellows were employed to urge the vapours forward. The needle being at zero, or thereabouts, on causing the mixed current to impinge upon the rocksalt, the needle immediately swings aside, the deflection varying from  $20^{\circ}$  to  $80^{\circ}$  and more, according to the delicacy of the galvanometer and the quality of the vapour.

From such experiments, which prove heat to be liberated when vapour comes into contact with the salt, the condensation of the vapour has been inferred. I accept the inference.

This, however, does not imply the acceptance of the inference from this inference, that the condensed films exert the action ascribed to them on radiant heat. To test whether they do so or not I had a circular plate of rocksalt mounted on its edge, and so placed that a beam of heat passed through it normally to a distant thermopile. The source of heat was an incandescent spiral, aided by a concave mirror; and the total radiation, after passing through the salt and impinging on the pile, produced a deflection of  $51^{\circ}$ . This radiation was accurately neutralised by a compensating cube, the needle under the operation of the two opposing forces pointing to  $0^{\circ}$ . By an arrangement which every experimenter can imagine for himself, sheets of air, laden with various vapours, could be poured in succession over the plate of salt. If, under these circumstances, absorbent films were formed, the equilibrium would be destroyed and the needle would move from  $0^{\circ}$ . My slit, which was the flattened base of an open tin cone, was placed across the upper part of the plate of rocksalt, so that the vapours, which were all heavier than air, should fall over the plate downwards. Here are the results obtained when the following vapours were permitted to form films upon the plate:—

Bisulphide of Carbon . . . . .	A barely sensible action.
Chloroform . . . . .	No action.
Benzol . . . . .	No action.
Iodide of Methyl . . . . .	No action.
Iodide of Ethyl . . . . .	No action.
Amylene . . . . .	No action.
Sulphuric Ether . . . . .	A barely sensible action.
Acetic Ether . . . . .	No action.
Formic Ether . . . . .	No action.
Alcohol . . . . .	No action.

The minute deflections produced by bisulphide of carbon and sulphuric ether had nothing to do with liquid films, so that the words "no action" might have been written against these substances as against the others. While therefore recognising the fact of condensation, these simple experiments prove how incorrect it is to credit the condensed films with the effects which have been ascribed to them. According to MAGNUS, alcohol exhibits a force of vapour-hesion particularly strong: but we here see that even this vapour produces no sensible effect. The vapours have been tested with other sources of heat, with the same result.

The deportment of dry and humid air is, as usual, very instructive. When the thin plate of rocksalt resting on the naked face of the pile, was exposed to the common air of the laboratory, it, of course, contracted a film corresponding to the humidity of the air. The sweeping away of this film by dry air produced a very small deflection indicating cold. When, on the contrary, humid air was urged against the salt, the deflection indicating heat was prompt and large. We have now to test the action of the liquid film thus formed upon radiant heat. The circular plate of rock-salt before referred to was mounted, with the incandescent spiral on one side and the pile on the other. The slit was so arranged that dry and humid air could be sent in succession over the surface of the plate. As before, the radiation from the spiral was neutralised by the compensating cube, the needle pointing to zero when the two sources were in equilibrium. On sweeping dry air over the plate of salt, so as to remove the film contracted from the laboratory air, there was no motion of the needle. On pouring humid air from the slit over the salt, there was no motion of the needle. To moisten the air it was urged from bottom to top through a tall jar filled with wet bibulous paper. The same apparatus had furnished humid air which produced a swing of  $80^{\circ}$  when urged against the thin plate of rocksalt resting on the face of the pile. As a barrier to radiant heat it was nevertheless powerless. The condensation may even be considerably enhanced without producing any sensible effect. Through a glass tube I urged my breath against the plate of salt so as to produce the colours of thin plates, without any sensible effect upon the galvanometer.

Having thus clearly shown what films, even in an exaggerated form, cannot

accomplish, I hope, in testing the action of humid air, that the use of the silvered tube, closed with polished plates of rocksalt, on which no trace of visible moisture is deposited, will be conceded to me. This tube involves the use of a source of heat of small dimensions. The lime light, though fulfilling this condition, is not suitable, because of the high refrangibility of its heat. The incandescent platinum spiral would be better; still, the radiation from this source is but feebly absorbed by the aqueous vapour taken up by air at ordinary temperatures. The oxyhydrogen flame fulfils the required conditions best.\* It has the advantage of high temperature and low refrangibility, while the fact that its heat, as coming from aqueous vapour, is absorbed with special energy, by aqueous vapour, is also a strong recommendation. In the Bakerian Lecture for 1864, I have illustrated this point. It was then shown that when a platinum spiral, rendered incandescent by a voltaic current, had 5·8 per cent. of its heat absorbed by un-dried air, a hydrogen flame had from 17 to 20 per cent. of its heat absorbed. The mere plunging of a platinum spiral into the flame caused the absorption to fall from 17 per cent. to 8·6 per cent. Hence my reason for choosing a hydrogen flame in the present instance.

Dry air and humid air being caused to occupy the experimental tube in succession, both of them were compared with the radiation through the tube when very perfectly exhausted by a BIANCHI'S pump. The following results were obtained.

	Deflection.	Absorption per 100.
Vacuum . . . . .	0·0°	0·0
Dry air. . . . .	0·0°	0·0
Humid air. . . . .	8·0°	11·7
Vacuum . . . . .	0·0°	0·0
Dry air. . . . .	0·0°	0·0
Humid air. . . . .	7·6°	11·2

The deflection through a vacuum, otherwise the total heat, was 47° which, according to my calibration table, is equivalent to 68 units.

A fresh supply of hydrogen was here introduced into the gas holder. The total heat being 46° or 65 units, the following results were obtained.

	Deflection.	Absorption per 100.
Dry air. . . . .	0·0°	0·0
Humid air. . . . .	6·2°	9·5
Dry air. . . . .	0·0°	0·0
Humid air. . . . .	6·7°	10·3

Mean of the four determinations with humid air 10·7.

\* I was careful to assure myself that, unless it amounted to the visible wetting of the plates of salt, there was no sensible stoppage of the rays from the oxyhydrogen flame. This quite agrees with the result obtained by MAGNUS himself, in the experiment with the concave mirror already referred to. Unless he visibly wetted the mirror he failed to impair the energy of the reflected beam.



A column of humid air 38 inches long absorbs, according to these experiments, 10·7 per cent. of the radiation from a hydrogen flame. I have been criticised for estimating the absorption of the earth's rays within 10 feet of the earth's surface at 10 per cent. This estimate I consider a moderate one, and the foregoing experiments prove it to be so.

It would be an error to suppose that determinations like these are easily made. They require the most scrupulous care for their successful accomplishment. The hydrogen issued from the gas holder through an orifice of fixed dimensions in a stream of the utmost possible constancy. It was then led into a Sugg's regulator, whence it issued under an absolutely constant pressure. The flame issued from a circular brass burner with an aperture  $\frac{3}{16}$ ths of an inch in diameter. It was carefully surrounded by a hoarding, the space within the hoarding being packed with horsehair. Every precaution, in fact, was taken to avoid the agitation of the air around the flame. Proper care was also taken to secure the pile against disturbance by air currents. The air being first purified, by passing it through caustic potash and sulphuric acid, was rendered humid by carrying it over wet bibulous paper contained in a suitable tube. It required some minutes to enter, and it was therefore necessary, by prior patient observance of the needle, to make sure that during this interval no change occurred in the radiation save that effected by the humid air itself. The humid air was removed from the experimental tube, not by exhaustion which always causes precipitation, but by gently forcing, by means of a compressing pump, dry air through the tube. When this was done, the needle, in all the experiments above recorded, returned within a small fraction of a degree to zero.\*

With the rough, wide experimental tube to which reference has already been made, I, ten years ago, found the absorption of a column of humid air 38 inches long, to be 8 per cent. of the total radiation from a flame of hydrogen.

### §. 6. *Conservation of Molecular Action.*

If the absorption of radiant heat be the act of the constituent atoms of compound molecules, its amount depending solely on the number of molecules encountered by the calorific waves, then whatever may be the changes of density which gases and vapours undergo, so long as the number of molecules remains the same, the absorption ought to continue constant. Such constancy, should it be proved to exist, I name the "conservation of molecular action." The experiments now to be described deal with this question.

Besides the silvered experimental tube already described as 38 inches long, I had another constructed of the same diameter, and with similar terminal apertures. Its length was 10·8 inches. The one tube was, therefore, 3·5 times the length of the

\* The temperature of the laboratory air during the foregoing experiments was 60° FAHR.

other. The shorter tube was constructed with the view of proving that the absorptions I had recorded in previous memoirs were exerted by the vapour molecules, and not by liquid layers deposited on my plates of salt. The hypothesis of such layers being, however, completely disposed of, we can carry the experiments a step further. Assuming that the absorption does not change with change of density, so long as the quantity remains constant, it would follow that 1 mercury inch of vapour in the long tube ought to quench as much heat as 3·5 inches in the short one. The same conclusion ought, of course, to hold good when we compare 2 inches of vapour in the long tube with 7 inches in the short one.

The experiments have been made, and with the following results :—

SULPHURIC ether vapour.

SHORT experimental tube.

Pressure.	Deflection.	Absorption per 100.
3·5 inches . . .	24°	30
7 „ . . .	30°	37·5
Total heat .	50°	

Again :—

3·5 inches . . .	24°	30
7 „ . . .	31·5°	39·4
Total heat .	50°	

Taking the means of these two experiments we have the absorptions—

For 3·5 inches . . . .	30 per cent.
For 7 „ . . . .	38·5 „

Such is the result obtained with the short tube : we now turn to the long one.

LONG experimental tube.

Pressure.	Deflection.	Absorption per cent.
1 inch . . . .	23°	30·3
Total heat .	49°	
2 inches . . . .	31°	38·8
Total heat .	50°	

These results are almost identical with those obtained with the short tube and greater pressures.

The source of heat in this case was a dull lime light. In subsequent experiments the light was brightened. Here is the result.

## LONG experimental tube.

Pressure.	Absorption.
1 inch . . . . .	22·3 per cent.
2 inches . . . . .	29·5 „

## SHORT experimental tube.

Pressure.	Absorption.
3·5 inches . . . . .	22·5 per cent.
7·0 „ . . . . .	30·0 „

The agreement here is almost as close as that established by the first experiment. With a still brighter source of heat the absorptions were :—

## LONG tube.

1 inch . . . . .	18·4 per cent.
2 inches . . . . .	25·7 „

## SHORT tube.

3·5 inches . . . . .	18·8 per cent.
7·0 „ . . . . .	25·6 „

When, therefore, the density of the vapour varies inversely as the length of it traversed by the calorific rays, the absorption remains constant.

The hydride of amyl lends itself conveniently to experiments of this character. With it, and with the lime light as source, the following measurements have been made :—

## HYDRIDE of amyl.

## LONG experimental tube.

Pressure.	Deflection.	Absorption.
1 inch . . . . .	10°	12·8
2 inches . . . . .	15°	19·2
Total heat	49·4°	

## SHORT experimental tube.

Pressure.	Deflection.	Absorption.
3·5 inches . . . . .	10°	12·2
7·0 „ . . . . .	15°	18·3
Total heat	50·5°	

The agreement here is close enough to illustrate the law; the greatest difference being under 1 per cent.

At this point the following entry appears in my note book :—"It might have been wise on my part to rest content with the comparison of the long and short tubes with the lime light as source of heat. But for the sake of completeness I wished to introduce the incandescent spiral. The fulfilment of this wish—that is to say, the successful performance of a single experiment—has cost me more than a week's work. Once however committed to the task, I could not leave it incomplete.

"The discrepancy between the two tubes was in no case great, hardly ever exceeding 2 per cent. But the difference was uniformly in favour of the long tube and small density. Diaphragms were employed, the position of the short tube was shifted, and it was finally placed so that the pile should occupy the same position in relation to its adjacent end as it did in relation to the adjacent end of the long tube. The discrepancies then disappeared, the absorptions in the two tubes proving practically identical.

"Many leaves of paper were covered with observations during the week, but it is useless to take up time and space in copying them here. One representative observation will suffice."

#### SULPHURIC ether.

Source of heat—bright red spiral with rocksalt lens.

##### LONG experimental tube.

Pressure.	Deflection.	Absorption.
1 inch . . . .	20·0°	23·5
2 inches . . . .	27·3°	32·1
Total heat	51·0°	

##### SHORT experimental tube.

Pressure.	Deflection.	Absorption.
3·5 inches . . . .	17·8°	23·4
7·0 „ . . . .	24·8°	32·6
Total heat	49·0°	

The agreement between the two tubes is as perfect as could be desired.

It is easy to record these experiments, but it is not so easy to make them. On every portion of the apparatus—the source, the tube, the thermopile, and the galvanometer—extraordinary care must be bestowed to make the experiments strictly comparable. The results were checked by taking the total heat after every experiment—a precaution which insured the detection of any variation on the part of the source. When the platinum spiral was used, the battery of ten GROVE'S cells, employed to render

it incandescent, had to be very carefully prepared, freshly amalgamated zinc plates being used in each fresh battery. The requisite deflection of a tangent compass being produced, it was kept constant by means of a rheochord throughout the day. When the battery showed signs of rapid falling it was always renewed. It would be tedious to dwell upon the precautions taken to protect the source and the pile from the least agitation of the air. Such precautions are essential, but their necessity and form must be learnt by each experimenter for himself.

### §. 7. *Thermal Continuity of Liquids and Vapours.*

I have amply illustrated by experiments, recently made, the correspondence which subsists between vapour absorption and liquid absorption, when the quantities of matter traversed in the two cases by the calorific rays are proportional to each other. This correspondence, as I have already stated, was established eighteen years ago. And though the result goes to the very core of the discussion which my researches have aroused, though in relation to that discussion they had, in my estimation, a weight and import greater than those of any other experiments published by me, they seem never for a moment to have attracted the attention of those who have taken part in the discussion. Here is a result, published in 1864, which illustrates the point now under consideration:—

		Absorption per 100.	
		Vapour.	Liquid.
Bisulphide of Carbon . . . . .	0·48	4·3	8·4
Chloroform . . . . .	0·36	6·6	25·0
Iodide of Methyl . . . . .	0·46	10·2	46·5
Iodide of Ethyl . . . . .	0·36	15·0	50·7
Benzol . . . . .	0·32	16·8	55·7
Amylene . . . . .	0·26	19·0	65·2
Sulphuric Ether . . . . .	0·28	21·5	73·5
Acetic Ether . . . . .	0·29	22·2	74·0
Formic Ether . . . . .	0·36	22·5	76·3
Alcohol . . . . .	0·50	22·7	78·6

The magnitude of the absorption in the liquids is far greater than in the vapours; because the quantity of absorbent matter is far greater in the former than in the latter; but the order of absorption is the same.

When the vapours are doubled in quantity the absorptions are considerably increased. When trebled they are still further augmented; in other words, they approach more and more in magnitude to the absorptions of the liquids; but the harmony as regards order is never disturbed. What then would occur if the vapours were so increased as to render the quantities of matter in the two states, not proportional, but *equal* to one another? This is the question with which I now propose to deal. At the time when the results above recorded were obtained, I thought it probable that if

a circular liquid layer of a given diameter could be vaporized in a tube of the same diameter, the absorption would remain unchanged. In other words, I thought that the liberation of the molecules from liquid cohesion would neither augment nor diminish their action upon radiant heat. Since 1864 this problem has been often in my mind. The wide silvered tube, I am happy to say, has rendered the solution of the problem possible.

It is only highly volatile liquids that lend themselves to this experiment, because from them alone can vapours be derived of sufficient density to produce liquid layers of practicable thickness. On the 22nd of last October the experiment was first attempted. The source of heat was the lime light, the rays of which were received by a concave mirror silvered in front, and sent in a nearly parallel beam through the experimental tube. At the end nearest the source the tube was provided with a diaphragm having a circular orifice 1 inch in diameter. At the other end was a diaphragm with an orifice  $\frac{1}{2}$  an inch in diameter. Beyond this was placed the thermopile furnished, not with its reflecting cone, but with a tube of brass (shown in fig. 3) 2 inches long, and blackened within. In this arrangement, the heat which reached the pile did not even approach the interior cylindrical surface. The total heat employed produced a deflection of 60 galvanometric degrees, which, when the tube was exhausted by a powerful BIANCHI'S air-pump, was accurately neutralised by a compensating cube. Liquid sulphuric ether was then placed in a large flask provided with a sound stop-cock, the object being to expose a considerable evaporating surface. The flask was plunged in water, with the view of keeping the liquid and its vapour at an approximately constant temperature. The air being carefully removed from the flask, it was attached to the experimental tube, and a quantity of vapour was allowed to enter sufficient to render a column 38 inches long equivalent to a liquid layer 1 millimeter in thickness. Two concurrent experiments made the deflection produced by the vapour

41°

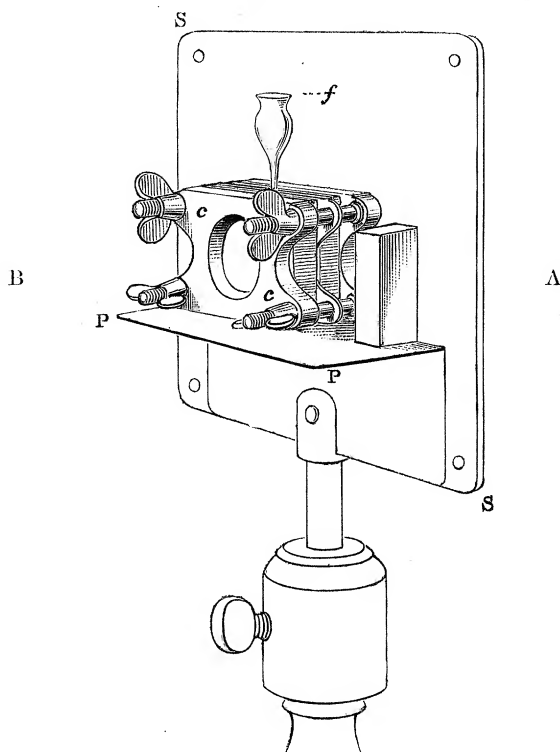
Without altering the quality of the heat, the absorption exercised by a liquid layer of sulphuric ether 1 millimeter thick was next determined. The rocksalt cell with which the experiment was made is described in detail in the Bakerian Lecture for 1864 (Phil. Trans., Vol. 154, p. 328.) The annexed figure (fig. 5) will give a sufficiently clear notion of its construction and disposition. Between two stout plates of brass, *c c*, and its fellow, two rocksalt plates of extreme purity are firmly clasped by suitable screws, due care being taken to protect the plates from a crushing pressure. The two brass plates referred to are perforated by circular apertures as shown in the figure. The two plates of salt are not allowed to come into contact but are separated from each other by a carefully worked brass plate 1 millimeter thick, perforated like *c c*. A portion of this middle plate is cut away, opening a passage into the interior of the cell. Through this passage the cell is filled with liquid by means of the funnel *f*. The cell is placed on a platform *P P* riveted on to the double brass screen *S S*. The source was placed at *A*, and the thermopile with its blackened tube at *B*. It is not necessary to figure them.

The needle being brought accurately to zero by the compensating cube when the cell was empty, liquid sulphuric ether was poured in. The consequent deflection was  $42^{\circ}$

Here vapour absorption and liquid absorption were so nearly alike as to stimulate me to further efforts. The entry in my note book on the 22nd ends with the remark: "I purpose repeating this experiment on Monday, with the view of rendering the result secure."

On Monday, accordingly, the experiments were resumed, but they proved by no means so easy as I had hoped to find them. For five days I worked at the subject without coming to any satisfactory conclusion. The source, the mirror, the cell, the experimental tube, and the thermopile, were all in turn objects of scrutiny; but there still remained a difference between the action of the liquid and that of its vapour sufficient to throw doubt on the assertion of their identity.

Fig. 5.



At the conclusion of many trials and precautions I found the absorption of the vapour still distinctly in excess of that of the liquid. I had reduced the spherical aberration to a minimum, by confining the reflection to a small central area of the silvered mirror. Still the image of the incandescent lime, formed at the end T' of the experimental tube, was large enough to encroach a little on the annular space surrounding the aperture closed by the plate of rocksalt. Diaphragms of polished metal had also been used to lessen the amount of heat falling upon the pile. I figured to

myself the heat impinging on the annular space and diaphragm, reverberated back to the end T of the experimental tube, reflected from the annular space and diaphragm at that end, and thus in part sent back to the pile. Such heat, instead of passing once through the vapour, would pass through it three times, and if it formed a sensible part of the total heat, might make vapour absorption appear greater than liquid absorption. I had the tube dismantled, and the annular spaces and diaphragms carefully coated with lampblack. Remounting the tube and measuring once more the vapour absorption, it was found to be

32.4 per cent.

This was the mean of five concurrent series of observations, in which every care was taken to ensure exactitude. Lest the total heat should vary, during the execution of a series, it was taken at the conclusion of every individual experiment.

The absorption of sulphuric ether, acting as a liquid, was next determined. The mean of three series of experiments, two of which yielded identical results, and the third of which differed only 0.7 per cent. from the others, made the absorption of the liquid ether to be

32.9 per cent.

which, I need not say, is surprisingly close to the vapour absorption, differing therefrom by only 0.5 per cent.

Informed by experiment that the heat from the incandescent platinum spiral was more powerfully absorbed than that of the lime light, I thought it worth while to inquire whether the liquid followed its vapour in absorptive energy, when the quality of the heat was changed. On Monday the 31st, accordingly, the rays from the spiral being rendered parallel by a rocksalt lens, the absorption of sulphuric ether was determined and found to be

66.7 per cent.,

while the absorption of the liquid was

67.2 per cent.

which again gives a difference of only 0.5 per cent.

On another occasion I found the absorption by sulphuric ether to be :

Vapour . . . .	71 per cent.
Liquid . . . .	70 „

On the 1st November I checked the result obtained with the lime light and mirror, by using the lime light and rocksalt lens. Here are the absorptions of the vapour and liquid respectively :—

Vapour . . . .	33.3 per cent.
Liquid . . . .	33.3 „

The absorptions are identical; while the result agrees closely with that obtained with the concave reflector.



When the requisite quantity of sulphuric ether vapour, viz. 7.2 mercury inches, was in the experimental tube, I tried whether the radiation from a LESLIE'S cube, coated with lampblack and filled with boiling water, could pass through the vapour. About 14 per cent. of the incident heat was transmitted. Had I been asked at the time whether a liquid layer of sulphuric ether 1 millimeter thick was pervious to the heat of the cube, I should have replied with some confidence in the negative. Hence, for the moment, I thought the experiment opposed to the law that vapour absorption and liquid absorption, when equal quantities of matter are compared, are the same. On actually testing a layer of the liquid ether 1 millimeter thick, the transmission of upwards of 6 per cent. of the incident heat was observed. So that in this case also we have harmony of deportment between liquid and vapour. The absorption of the vapour exceeds that of the liquid because the heat from the cube radiated freely against the interior silvered surface of the experimental tube, and by its reflection from that surface had its path through the vapour augmented in length. This augmentation naturally carried with it an increase of the absorption.

The next substance examined was hydride of amyl, the boiling point of which is 30° FAHR., or 5° lower than that of sulphuric ether. When a large evaporating surface is exposed, there is therefore no difficulty in obtaining, from this liquid, vapour of a pressure of 6.6 inches of mercury. This, in a tube 38 inches long, would, if squeezed to liquefaction, produce a layer 1 millimeter thick. Vapour absorption and liquid absorption being measured in succession, this is the behaviour of the hydride of amyl:—

Absorption by vapour . . . . 51 per cent.

Absorption by liquid . . . . 51 per cent.

the two absorptions being absolutely identical.\*

Combining this section and the last, their joint results may be thus summed up. Beginning with a column of sulphuric ether vapour 38 inches long at 7.2 inches pressure, or with a column of hydride of amyl vapour 38 inches long and at 6.6 inches pressure, and gradually shortening the column without altering the quantity, the vapour would gradually augment in density and pass wholly, when reduced to a thickness of 1 millimeter, into the liquid state of aggregation. Suppose a beam of heat of constant value, after passing through the vapour, to impinge upon a thermopile and to produce a definite galvanometric deflection; this deflection would remain absolutely fixed during all the changes of density and aggregation which we have

\* When the rocksalt cell was empty, reflection of course occurred at its two interior surfaces. A perfectly diathermanous liquid, with the refractive index of rocksalt, would annul this reflection. And though the liquids actually employed had a smaller refractive index than rocksalt, and though they were far from being perfectly diathermanous, their introduction into the cell must nevertheless have diminished the reflection and thus added to the transmitted heat. This addition, having been determined by calculation, was sensibly neutralised by the introduction of washers of thin note paper which slightly augmented the thickness of the liquid stratum traversed by the calorific rays.

supposed the vapour to undergo. In other words—as regards the absorption of radiant heat, the vapour would pass, without breach of continuity, through all its stages of condensation into the liquid form of matter.

A general law of molecular physics is, I apprehend, here illustrated.

### §. 8. *Rhythmic Absorption of Radiant Heat by Gases and Vapours.*

Conclusive as the foregoing experimental argument must appear, as regards the action of free molecules upon radiant heat, I am nevertheless glad to supplement it by another of a totally different character. On the 29th of November, 1880, I had the pleasure of witnessing, in the laboratory of the Royal Institution, the remarkable experiments of Mr. GRAHAM BELL, wherein musical sounds were evoked by causing an intermittent beam of light to impinge upon thin discs of various kinds of matter. I was soon convinced that the effects were due to the rhythmic gain and loss of heat. Being occupied with experiments on gases and vapours at the time, I thought that they might be invoked to decide the nature of the action revealed by Mr. BELL. The result was mentally clear before the experiment was made. I pictured a highly absorbent vapour exposed to the shocks of the intermittent beam, suddenly expanding during the moment of exposure, and as suddenly contracting when the beam was intercepted. Pulses of an amplitude probably far greater than those obtainable with solids would, I thought, be thus produced; and these pulses, if caused to succeed each other with sufficient rapidity, would be sure to produce musical sounds.

This idea was tested and verified on the spot. The Journal of Telegraph Engineers for December 8th, 1880, contains the following record of what occurred. “When Professor BELL was good enough to show me his experiments, I happened to be myself experimenting on the action of vapours upon radiant heat. Old experiments had revealed, and new ones had confirmed the fact that, as regards the absorption of heat, there existed vast differences between vapours. This is well illustrated by the deportment of bisulphide of carbon and of sulphuric ether, one of which is highly transparent, and the other highly opaque to radiant heat. It occurred to me that, if the action were due to the absorption of heat, we might possibly extract musical sounds from sulphuric ether vapour, whereas bisulphide of carbon vapour being transparent to heat-rays they would for the most part go through this vapour unabsorbed, and produce no sonorous effect. I think Professor BELL will bear me witness as to the result. We placed a quantity of sulphuric ether vapour in a test tube, and allowed an intermittent beam of light to strike upon the vapour far above the liquid, and we heard distinctly a musical tone of a pitch corresponding to the rapidity of the flashes. We then took the bisulphide of carbon vapour, and tried it in a similar manner, but neither Professor BELL nor myself could hear any trace of a musical sound.”\*

\* Mr. BELL has given a perfectly accurate account of this occurrence in the Philosophical Magazine,

It was obvious, however, that the arrangement of Mr. BELL—a truly beautiful one—was not suited to bring out the maximum effect. He had employed a series of glass lenses to concentrate his beam, and these, however pure, would, in the case of transparent gases, absorb a large portion of the rays most influential in producing sound. This may be illustrated by comparing a rocksalt lens, in my collection, with a glass lens of the same focal length prepared in the workshop of M. DUBOSCQ. Transmitted through the former, the radiation from an incandescent platinum spiral produced a galvanometric deflection of  $55^\circ$ , possessing, according to the table of calibration, a value of more than 100. Transmitted through the latter, the deflection fell to  $10^\circ$ , or to less than  $\frac{1}{10}$ th of the radiation transmitted by the rocksalt. The  $\frac{9}{10}$ ths here shown to be intercepted by the transparent glass, consist of heat on which transparent gases and vapours would exert a specially absorbent power. Hence the desirability of maintaining this important factor, in the radiation employed to test the sonorous power of such substances.

It was with the view of preserving intact these powerful calorific rays that I employed in my experiments on calorescence\* small concave mirrors silvered in front; and to these mirrors I now resorted. My more intense sources of heat comprised a SIEMENS' lamp connected with a dynamo machine; an ordinary electric lamp connected with a voltaic battery; and a lime light, produced sometimes by the combustion of oxygen and hydrogen, and sometimes by oxygen and coal gas. The lime light (which was used by me in 1859) is so handy, steady, and otherwise effective, that I have applied it almost exclusively throughout this part of the inquiry. Sources of heat, however, of much lower temperature than the lime light, have proved competent to evoke musical sounds. A candle flame, a red hot coal, a red hot poker, the same poker at the temperature of boiling water, and an incandescent platinum spiral, have all been proved effective, though of course far less so than the concentrated lime light.†

To produce the required intermittence I first employed a circle of sheet zinc 16 inches in diameter provided with radial slits. This was afterwards exchanged for a second disc of the same diameter, but furnished with circumferential teeth and interspaces. The disc was mounted vertically on a whirling table, and caused to rotate across the beam near the focus of the concave mirror. Immediately behind the disc was placed the flask containing the gas or vapour to be examined, while an india-

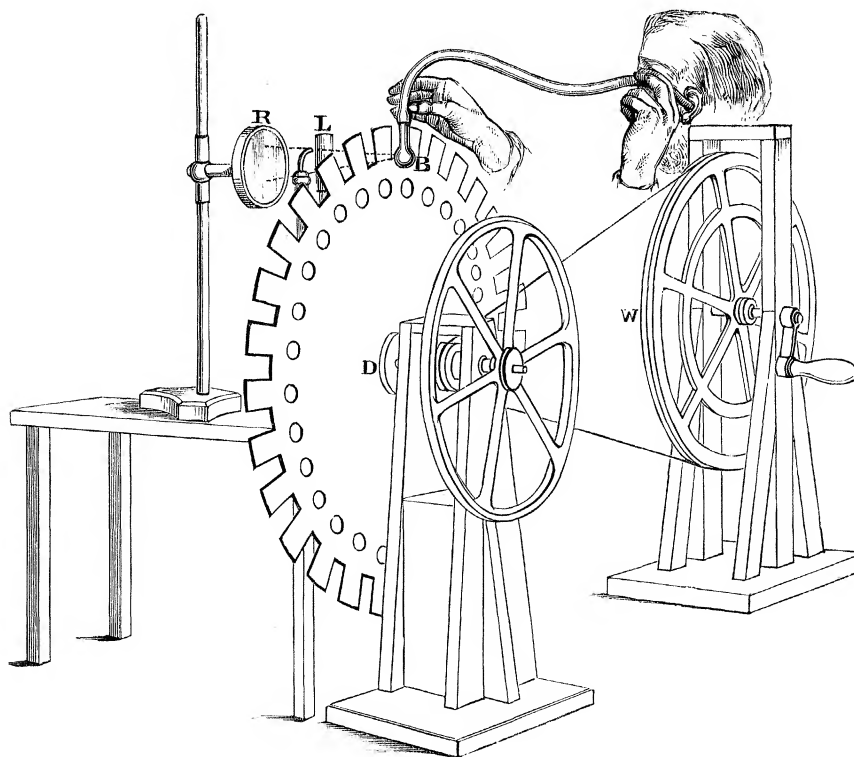
vol. xi., p. 519. With reference to what occurred on the 29th of November he writes thus:—"Professor TYNDALL at once expressed the opinion that the sounds were due to rapid changes of temperature in the body submitted to the action of the beam. Finding that no experiments had been made at that time to test the sonorous properties of different gases, he suggested filling one test-tube with the vapour of sulphuric ether (a good absorbent of heat), and another with the vapour of bisulphide of carbon (a poor absorbent); and he predicted that, if any sound was heard, it would be louder in the former case than in the latter. The experiment was immediately made; and the result verified the prediction."

\* Philosophical Transactions, 1866, Vol. 156, p. 1.

† These earlier experiments will be found recorded in the Proceedings of the Royal Society, vol. 31, pp. 307, 478.

rubber tube, ending in a hollow cone of ivory or boxwood, connected the flask with the ear. With this arrangement, simple as it is, sounds of surprising intensity were obtained with all those gases and vapours which my previous experiments with the experimental tube and thermopile had proved to be powerful absorbers of radiant heat. The final arrangement was that shown in fig. 6.

Fig. 6.



The source of heat is the carefully worked and centred lime-cylinder L, heated by the oxy-hydrogen flame. The rays from this source are received by the concave mirror R, and converged upon the bulb B which contains the substance to be tested. The bulb is connected with the ear by a piece of india-rubber tubing, ending in a tapering tube of boxwood or ivory. The intermittence of the calorific beam is effected by the disc D of strong cardboard, 2 feet in diameter, and provided at the circumference with 29 teeth and corresponding interspaces.\* The disc is caused to rotate by the wheel W, with which it is connected by a band. The positions of the sonorous bulb and of its ear-tube are shown in the figure. In the case of gases lighter than air the bulb B is turned upside down. With the heavier gases it is held erect. When vapours are tested, a small quantity of liquid is poured into the bulb, which is shaken

\* Intermittence is sometimes produced by the series of equidistant circular apertures shown in the figure.

so as to diffuse the vapour in the air above the liquid. The bulb is held so that the point of maximum concentration of the beam falls upon it.

With this apparatus I have tested more than once the sounding power of ten gases and of about eighty vapours. As a sound producer chloride of methyl is supreme. It is however closely followed by aldehyde, olefiant gas and sulphuric ether, the two latter being very nearly equal to each other. The volatility of the liquid from which the vapour is derived is of course an important factor in the result. For, however high the inherent capacity of the molecule as an absorber may be, if the molecules be scanty in number the effect is small. Feeble vapours, on the other hand, may to some extent atone by quantity for the inherent weakness of their molecules. A few examples will suffice to show how the specific action of the molecules over-rides the effect of volatility. Bisulphide of carbon with a boiling point of  $43^{\circ}$  C. is less powerful than acetic ether with a boiling point of  $74^{\circ}$ . Tetrachloride of carbon boils at  $77^{\circ}$  but its sound by no means equals that of acetal which boils at  $104^{\circ}$ . Chloroform with a boiling point of  $61^{\circ}$  is less powerful as a sound producer than valeral with a boiling point of  $100^{\circ}$ , or even than valerianic ether with a boiling point of  $144^{\circ}$ . Cyanide of methyl boils at  $82^{\circ}$ , but produces less sound than acetate of propyl with a boiling point of  $102^{\circ}$ . In the experimental tube, these vapours follow, as absorbers, the order of their sounds. When tested in liquid layers they follow the same order. I have examined about a score of liquids with boiling points varying from  $163^{\circ}$  to  $308^{\circ}$ . At ordinary temperatures the vapours of these liquids were practically inaudible. The liquids being plunged in a bath of heated oil the vapours so produced emitted, for the most part, powerful sounds. The measured absorptions of a sufficient number of substances, in relation to their sounding power, shall be tabulated immediately.

The fact is worth a passing reference that the chlorides of the elements appear one and all to be feeble sound producers, because they are one and all feeble absorbers of radiant heat. Many years ago I had found them highly diathermanous, and accepted chloride of sodium as representative of the class. Silicium chloride, for example, though very volatile is weak as a sound producer. Tetrachloride of carbon, and terchloride of phosphorus are also volatile, but not strong. Bichloride of tin, chloride of arsenic, chloride of titanium, and chloride of sulphur, are all feeble sound producers. In these three cases the boiling points are high, but non-volatility is not the cause of the weakness, for when the vapours are raised, by heating their liquids, almost to the pressure of the atmosphere, they are still but feebly sonorous. Whatever then the condition may be which renders these substances pervious to radiant heat, it appears to be a condition common to them all.

In experiments with the chlorides care must be taken to abolish all fumes. Bichloride of tin sounds loudly with fumes, but is weak without them. Simply heating the upper part of the flask frequently suffices to lower the sounds from loudness almost to silence.

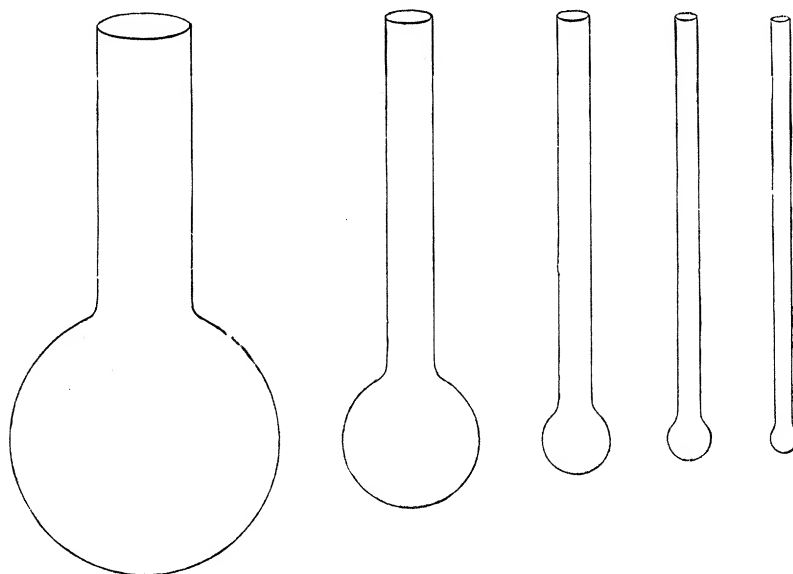
The universality of its presence, and the discussions which it has provoked, rendered the action of water vapour especially interesting to me. I did not imagine at the outset that the modicum of vapour diffused in atmospheric air at ordinary temperatures could produce sonorous pulses of sensible intensity. In my first experiment, therefore, I warmed water in a flask nearly to its boiling point. I heated the flask above the water with the spirit lamp flame, thus dissipating every trace of haze, and then exposed the clear vapour to the intermittent beam. The experiment was a virtual question put to the vapour as to whether I was right or wrong in ascribing to it the power of absorbing radiant heat. The vapour answered by emitting a musical note which, when properly converged upon the tympanum, seemed as loud as the peal of an organ. When the temperature was lowered from  $100^{\circ}\text{C.}$  to  $10^{\circ}\text{C.}$ , the sound did not vanish, as I expected it would. It remained not only distinct but strong. The flasks employed in these experiments were dried in a variety of ways, of which I have already given some account, and which will suggest themselves to every experimenter in this field. Taken open from the laboratory, and exposed to the intermittent beam, the flasks are always to some extent sonorous. Placed beside sulphuric acid underneath the receiver of an air-pump, and permitted to dry there, they are reduced to silence. The slightest invasion of humid air renders them again sonorous. Breathing for a moment into a dried and silent flask, a loud sounding power is immediately manifested.

Flasks without lips have been specially blown for these experiments, the india-rubber tubing being readily pushed over their necks. Large flasks are not the most suitable. To produce effective pulses sudden and intense expansions and contractions are required, and these are best obtained when the beam, at its place of maximum concentration, covers a large portion of the matter in the flask. Thin bulbs about a cubic inch in volume are both handy and effective; but the bulb may be reduced to  $\frac{1}{50}$ th, or even  $\frac{1}{100}$ th of a cubic inch, without rendering the sound insensible. A speck of water introduced into such tiny bulbs, when vaporised by heat, produces sounds which are not only sensible but loud. A series of bulbs which I have actually employed in my experiments are represented in their natural dimensions in fig. 7.

It cannot be necessary to state that the absorption which produces the pulses is direct and immediate, being the act of the gaseous molecules. The pulses are not due to the heating of the glass envelope and the communication of its heat to what it contains. For, were this the mode of heating, air would be as sonorous as olefiant gas. Nor are the pulses due to the sudden vaporization of a liquid layer which might be supposed to overspread the interior of the flask. When water at a low temperature is purposely caused to cover the interior surface, exposure to the beam produces sound of a certain intensity. When the flask is so heated in a spirit flame as to chase away every trace of the adherent liquid, the exposure of the pure vapour, then within the flask, to the beam, generates a sound far louder than that produced when the liquid film was there. Holding the bulb containing the hot vapour for a little time in the

intermittent beam, its temperature falls ; the quantity of vapour diminishes, and the sound sinks in intensity. On quitting the spirit flame, the bulb in some cases must have been near a red heat, but even at this temperature the vapour sounded loud.

Fig. 7.



It has, I think, been amply shown that when the molecules of a liquid are rendered free by vaporization they carry with them their absorbent power, liquids and vapours being pervious and impervious to the same quality of heat. Hence the inference, that prior transmission through a liquid of sufficient thickness ought so to sift a calorific beam as to render it powerless to act on the vapour of that liquid. Even with the loudest sounding vapours this proves to be the case, a layer of liquid  $\frac{1}{8}$ th of an inch thick being found generally sufficient to deprive the beam of its efficient rays, and the vapour of its sounding power.

In transparent liquids, the visible rays have free transmission, the destruction of sounding power by such liquids must, therefore, be due to the absorption of the invisible calorific rays. This induction, which hardly needs verification, is nevertheless capable thereof. Many years ago I pointed out the astonishing transparency of dissolved iodine to the invisible heat rays. Placed in the path of the intermittent beam, a layer of this substance, perfectly opaque to light, does not sensibly diminish the sound of transparent gases and vapours. To such substances, the iodine is exactly complementary, arresting the rays which they transmit, transmitting the rays which they absorb, and, therefore, not interfering with the sounding power.

That sounds may also be produced by the absorption of the visible rays is well exemplified by the deportment of iodine and bromine vapours, both of which yield with the lime light forcible sounds. Here the intervention of a transparent liquid,

however adiathermanous it may be, produces no sensible effect upon the sound, the reason being that it permits the particular rays which act upon the coloured vapours to pass freely through it. A layer of dissolved iodine, on the other hand, deprives the beam of its power of evoking sounds from either iodine or bromine vapour.

The rotation which produces the maximum effect is soon ascertained by experiment. The sound is loudest when the pulses succeed each other in periods which invoke the resonance of the flask. I possess a hollow cone with a well-polished rocksalt base, by which this point is well illustrated. Filling this cone with chloride of methyl, while the base is turned towards the source of heat, the apex of the cone being connected by a tube with the ear, sounds of extraordinary intensity are produced. Abandoning the ear-tube, the sound can be heard at a distance. But to obtain this effect the speed of rotation must be definite and constant. The maximum sound once obtained, either the lowering or the heightening of the speed rapidly enfeebles it. It is difficult by hand-turning to keep the rate of rotation constant. Hence the desirability of a mechanical arrangement, which would ensure the proper rapidity and necessary uniformity. One or two motive powers have been tried, including a small steam-engine and an electro-magnetic engine, but the arrangement has not yet been brought to perfection.

### §. 9. *Manometric measurements.*

Some time before the visit of Mr. GRAHAM BELL in November, 1880, I had inserted into my old experimental brass cylinder a narrow tube of glass, which being bent at a right angle a few inches above the cylinder could hold an index of coloured liquid in its horizontal portion. I had long known that the absorption of radiant heat must be accompanied by the expansion of the absorbing body, but thought that such expansion would furnish only a rough measure of the absorption. With ordinary sources of heat I found the expansion small, even when sulphuric ether occupied the experimental tube; but when a pair of stout carbons, rendered incandescent by a SIEMENS' machine, were employed as a source, the liquid index was driven forcibly out of the narrow glass tube.

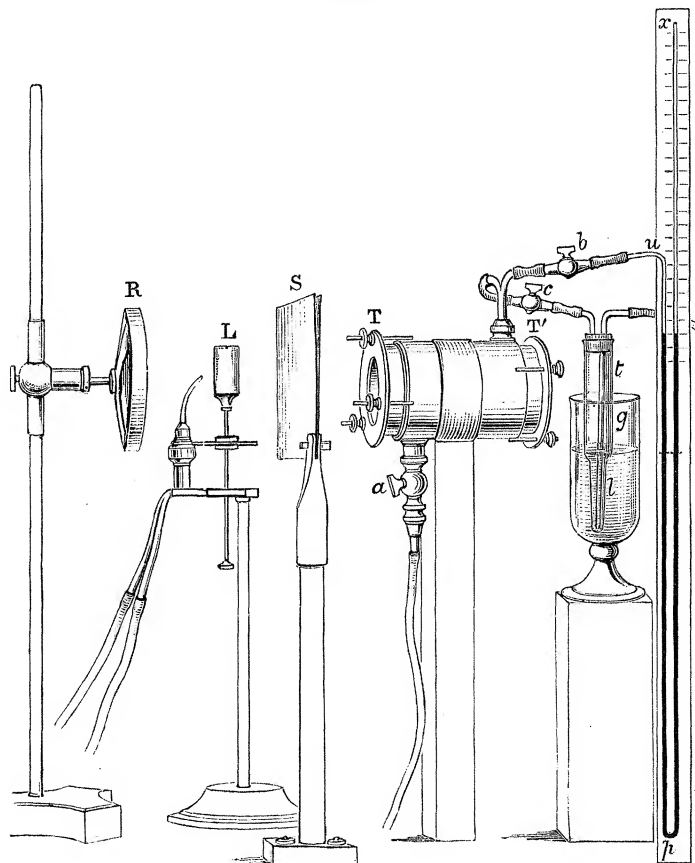
The experimental tube, however, was but a rude manometer, and I therefore sketched and described to my assistant at the time, with a view to its construction, a handier instrument. The apparatus was to consist of a short tube with rocksalt ends, capable of being exhausted and filled with any required gas or vapour. Through this tube it was proposed to send a concentrated calorific beam, whose action on an absorbent gas or vapour should be declared by the depression of a liquid column in one leg of a U tube, and its elevation in the other. Two rocksalt plates were to be employed with the view of allowing the beam free escape from the tube after it had done its work upon the gas or vapour. The warming of the apparatus by the reverberation of the heat would be thus avoided. The point aimed at was to effect the expansion of



the gaseous body purely by radiant heat, and undisturbed as far as possible by heat derived from the envelope.\*

A number of manometric tubes of different lengths and materials were constructed on this principle, some being of glass and some of metal. The instrument with which the measurements now to be recorded were executed is represented in fig. 8. T T' is

Fig. 8.



a glass tube 4 inches long and 3 inches in diameter. It is provided with brass flanges at the ends which reduce the diameter to 2.5 inches. Against these flanges, transparent plates of rocksalt are fixed air-tight. The tightness of the tube was secured, sometimes by india-rubber washers properly greased, and sometimes by cement.† A stop-cock *a*

\* Professor RÖNTGEN was, I believe, the first to turn the expansion of gases to account in demonstrating the absorption of radiant heat. The very day, moreover, on which I made my communication to the Society of Telegraph Engineers, viz. the 8th of December, 1880, he forwarded to a scientific journal the announcement of his having obtained sounds from coal-gas and ammonia (see WIEDEMANN'S *Annalen*, Jan. 1881). His subsequent experiments with aqueous vapour, &c., agree with mine.

† The absorption of the vapours by india-rubber—which was in some cases extraordinary—caused the washers to be abandoned.

near one end of T T' was connected with a barometer tube and an air-pump. A T-piece at the other end was connected on the one side with a purifying apparatus (not shown), consisting of two U tubes, one containing fragments of Carrara marble wetted with caustic potash, the other containing fragments of glass wetted with sulphuric acid. Before entering these U tubes the air was freed from suspended matter by a plug of cotton wool. On the other side the T-piece was connected with a quill tube of glass bent into the shape of a U, in the two legs of which a coloured liquid stood at the same level. The liquid column when standing at the same level in both arms of the U was 350 millimeters high in each, while the free leg of the U rose to a height of about 500 millimeters above the surface of the liquid (shortened in the figure). The source of heat was the lime cylinder L, rendered incandescent by a flame of coal gas and oxygen. The rays from the lime cylinder were received by a concave mirror R silvered in front, and sent by it in a convergent beam through the manometer tube. The focus of the beam was within the tube and near its most distant end. The gas and oxygen were supplied from gasholders specially constructed for these and similar experiments; long and futile experience of gas from the public mains, or compressed in iron bottles, having shown independent gasholders which could be kept at an unalterable pressure to be essential.

The experiments were conducted thus:—A test-tube *t*, plunged in water, held by the glass *g*, contained the liquid whose vapour was to be examined. Through a cork which stopped the test-tube passed a narrow tube of glass, ending in a small orifice near the bottom of the test-tube, and at a considerable depth below the surface of the liquid. To augment this depth, and to economise the liquid, the lower part of the test-tube was drawn out to half the diameter of its upper part. A second narrow tube passed also air-tight through the cork, and ended immediately beneath it. Both tubes were bent at a right angle above the cork. The manometric tube being exhausted, air freed from its carbonic acid, its moisture, and its suspended matter, was allowed to bubble through the liquid in the test-tube, and to pass thence into the manometric tube. To spare the oxygen in the gasholder it was cut off during the interval between two consecutive experiments, the coal gas being kept continually alight. When the manometric tube was filled, which was always accomplished through an orifice of fixed dimensions, the oxygen was turned on, and the cylinder was allowed to remain for one minute under the action of the intensified flame. During this time a double silver screen S intercepted the radiation. At the end of a minute this screen, which moved on a hinge, was withdrawn, the beam then passing through the mixed air and vapour. The liquid standing in the adjacent leg of the narrow U-tube was immediately depressed, that in the opposite leg being equally elevated. The rise of this latter column above its starting point, marked zero on a millimeter scale, was accurately measured. Double this rise gave the difference of level in the two legs of the U, and this “water pressure” expressed the augmentation of elastic force by the absorption of radiant heat.

Here follow a certain number of the measurements which have been thus made. They do not comprise the whole of the substances examined.

TABLE V.

## VAPOURS.

INCREASE of elastic force by Radiant Heat.

Name of Liquid.	Boiling point.	Mean Water pressure.	Character of sound.
1. Sulphuric Ether . . . . .	35°	300 millims.	Very strong
2. Hydride of Amyl . . . . .	30°	279 "	"
3. Acetone . . . . .	58°	267 "	"
4. Bromide of Ethyl . . . . .	39°	264 "	"
5. Formic Ether . . . . .	55°	261 "	"
6. Acetic Ether. . . . .	74°	248 "	"
7. Acetal. . . . .	104°	237 "	"
8. Chloride of Allyl . . . . .	46°	235 "	"
9. Iodide of Methyl . . . . .	45°	233 "	"
10. Dichloride of Ethidene . . . . .	57°	217 "	Strong
11. Nitrate of Ethyl . . . . .	86°	208 "	"
12. Nitrite of Amyl . . . . .	99°	205 "	"
13. Chloride of Butyl . . . . .	69°	185 "	"
14. Butyric Ether . . . . .	121°	183 "	"
15. Formic Acid . . . . .	99°	180 "	"
16. Valeral . . . . .	100°	172 "	"
17. Valerianic Ether . . . . .	144°	168 "	"
18. Acetate of Propyl . . . . .	102°	166 "	"
19. Methylic Alcohol . . . . .	—	162 "	"
20. Iodide of Ethyl. . . . .	72°	148 "	Moderate
21. Bromide of Butyl . . . . .	92°	134 "	"
22. Dutch Liquid . . . . .	85°	127 "	"
23. Acetate of Butyl . . . . .	114°	120 "	"
24. Benzol. . . . .	81°	117 "	"
25. Carbonic Ether. . . . .	126°	108 "	"
26. Chloride of Amyl . . . . .	102°	105 "	"
27. Chloropierin . . . . .	112°	94 "	"
28. Iodide of Allyl . . . . .	101°	92 "	"
29. Chloroform . . . . .	61°	89 "	"
30. Iodide of Butyl. . . . .	121°	88 "	"
31. Allylic Alcohol . . . . .	97°	84 "	"
32. Bisulphide of Carbon. . . . .	43°	81 "	"
33. Bromide of Amyl . . . . .	119°	78 "	"
34. Cyanide of Ethyl . . . . .	98°	77 "	"
35. Butyl Alcohol . . . . .	110°	72 "	Weak
36. Nitrate of Amyl . . . . .	147°	67 "	"
37. Oxalate of Ethyl . . . . .	—	66 "	"
38. Cyanide of Methyl. . . . .	82°	64 "	"
39. Tetrachloride of Carbon . . . . .	77°	58 "	"
40. Bromoform . . . . .	150°	44 "	"
41. Xylol . . . . .	140°	44 "	"
42. Amylic Alcohol. . . . .	130°	42 "	"

TABLE V (continued).

Name of Liquid.	Vapours Boiling point.	Mean Water pressure.	Character of sound.
43. Iodide of Amyl. . . . .	146°	42 millims.	Weak
44. Terebine . . . . .	160°	39 "	"
45. Cymole . . . . .	175°	38 "	"
46. Butyric Acid . . . . .	163°	Very small absorptions and very feeble sounds at ordinary temperatures. Sounds in most cases very strong when liquid is heated to its boiling point.	
47. Butyrate of Amyl. . . . .	176°		
48. Caprylic Alcohol . . . . .	180°		
49. Valerianic Acid. . . . .	175°		
50. Pure Aniline . . . . .	184°		
51. CEnanthic Ether . . . . .	188°		
52. Valerianate of Amyl. . . . .	196°		
53. Salicylous Acid. . . . .	196°		
54. Caproic Acid . . . . .	205°		
55. Nitro Benzol. . . . .	205°		
56. Kreosote . . . . .	210°		
57. Menthol . . . . .	213°		
58. Chinoline. . . . .	238°		
59. Eugenol . . . . .	247°		
60. Nicotine . . . . .	250°		
61. Monobromnaphthaline. . . . .	277°		
62. Sebasic Ether . . . . .	308°		

TABLE VI.

## GASES.

Name of gas.	Water pressure.
Chloride of Methyl. . . . .	350 millims.
Aldehyde . . . . .	325 "
Olefiant Gas . . . . .	315 "
Sulphuric Ether . . . . .	300 "
Nitrous Oxide . . . . .	198 "
Marsh Gas. . . . .	164 "
Carbonic Acid . . . . .	144 "
Carbonic Oxide . . . . .	116 "
Oxygen . . . . .	5 "
Hydrogen . . . . .	5 "
Nitrogen . . . . .	5 "
Dry air. . . . .	5 "
Humid air at 50° C. . . . .	130 "

Sulphuric ether is here inserted with the view of connecting this Table with the last. Of all gaseous bodies hitherto examined chloride of methyl is the most energetic absorber and the most powerful sound producer. After it comes aldehyde, with a

boiling point of  $21^{\circ}$  C. The figure 5 attached to the elementary gases, and to dry air, expresses, not absorption of radiant heat, but expansion, due to contact with the slightly warmed apparatus. The nitrous oxide employed was derived from an iron bottle in which it was preserved for medical purposes. In some of my experiments marsh gas showed itself a better absorber than nitrous oxide. This, for instance, was the case in experiments made in the spring of 1880 with the manometer. The sample of marsh gas wherewith the foregoing result was obtained was very carefully prepared in our chemical laboratory.

The temperature of  $50^{\circ}$  C. in the case of humid air was obtained in a wooden shed erected in our laboratory. The shed is traversed by two tubes of sheet iron 4 inches in diameter, which carry the heated air and products of combustion from two large ring-burners. It is 8' 6" long, 4' 3" wide, and 7' feet high. The temperature of the air within it can be readily raised to  $60^{\circ}$  C. In the experiment recorded in Table VI. the air was taken from the outside laboratory through a tube passing through the wooden wall of the shed. It was caused to bubble through water contained in a large flask which had been permitted to remain for some time in the warm shed. The mixed air and vapour entered the manometer tube at a temperature some degrees lower than that of the tube itself. Closely examined, all parts of this tube were bright and dry when the vapour-laden air was within it. On permitting the beam from the lime light (produced by coal-gas and oxygen) to pass through the mixture, a prompt rise of 65 millimeters was the consequence. Cutting the beam off the column rapidly returned to zero. The double of 65, or 130 millimeters, gives the difference of level in the two legs of the U-tube.

I have done my best to render these determinations correct. They have been repeated both by myself and my assistant\* a great number of times. The first measurements were made in the early part of last year, and were made known in the Royal Institution on the 8th of April, 1881. Difficulties were encountered in obtaining a powerful, and at the same time constant, source of heat. The mixture of coal-gas and oxygen issuing from independent holders was finally resorted to. The sounds are classified into "very strong," "strong," &c., but it is, of course, impossible to say where one class ends and another begins. They shade gradually into each other. But if the middle members of any class be compared with the corresponding members of another class, the difference of sounding power will appear.

#### §. 10. *Application of Results to Meteorology.*

If it be at length conceded that aqueous vapour exerts upon radiant heat the action which I so long ago ascribed to it, I think the knowledge of this action will prove of importance to the scientific meteorologist. Meteorology, as connected with heat, seems to me to abound in facts which it has hitherto been incompetent to

\* Who has aided me in this investigation with his usual zeal and intelligence.

explain. This, for example, I hold to be the case as regards the celebrated observations of PATRICK WILSON of Glasgow, made a century ago. WILSON brought strongly into light the great differences which sometimes exist between the temperature of the earth's surface, and of the air at a small elevation above the surface. His letter to Dr. MASKELYNE on this subject is published in the Philosophical Transactions for 1780 under the title:—“*An account of a most extraordinary degree of cold at Glasgow, together with some new experiments and observations on the comparative temperature of hoar frost and the air near it.*” On the afternoon of the 13th of January, 1780, the cold was intense, a thermometer at the high window of the observatory pointing, at 7 P.M., to  $0^{\circ}$  FAHR. At 8 P.M. WILSON and Dr. IRVINE laid two thermometers upon the snow, and hung up two others in the air 2 feet above the snow. Here follow the temperatures observed on the evening of the 13th and on the morning of the 14th of January:—

Time of observation.	Snow temperature.	Air temperature.
$8\frac{1}{2}$ P.M.	$-12^{\circ}$	$-0^{\circ}$
9 „	$-14^{\circ}$	$-2^{\circ}$
10 „	$-14^{\circ}$	$-4^{\circ}$
11 „	$-17^{\circ}$	$-6^{\circ}$
$11\frac{1}{2}$ „	$-18^{\circ}$	$-6^{\circ}$
$\frac{1}{2}$ A.M.	$-20^{\circ}$	$-8^{\circ}$
1 „	$-23^{\circ}$	$-7^{\circ}$

The sign — signifies that the temperatures were all below zero FAHRENHEIT. These temperatures amply justify WILSON's statement that the cold was “extraordinary.” Coexistent moreover with the general cold we have a difference of  $16^{\circ}$  between the temperature of the surface and that of the air 2 feet above it. Had the air thermometer been hung 10 feet, instead of 2 feet, above the surface the difference would have been still greater. The thermometer, moreover, must have been chilled, not only by its immersion in cold air, but also by its own radiation against the intensely cold snow. The chilling of the superficial snow was purely an effect of radiation. Beneath the surface its temperature reached  $+14^{\circ}$ . WILSON filled a bread-basket with this warm snow at  $2\frac{1}{2}$  A.M. on the 14th. Within half an hour it had fallen  $24^{\circ}$ , and in two hours  $32^{\circ}$ .

I venture to predict that if WILSON's experiment be repeated during the cold of a Canadian winter the same result will be obtained; and it seems to me that until the action of water vapour upon radiant heat had been discovered no explanation of the phenomenon could have been given. It was accepted but not accounted for. On the night of WILSON's observations “a light air was felt coming from the east.” With such an “air” and such a temperature the quantity of water vapour in the atmosphere must have been infinitesimal. Dry air being a practical vacuum to the rays of heat, were the vapour-screen entirely removed, the earth would find itself exchanging tem-

peratures with celestial space, and the superficial chill would be commensurate. In WILSON's case, though the vapour was not abolished, it was so far diminished as to produce the observed refrigeration. Meteorologists, I am informed, sometimes say that laboratory experiments, however well performed, have but little application to their field of observation.\* I, on the other hand, submit that such experiments are necessary to rescue their science from empiricism. What could WELLS have done with dew had he not been preceded by LESLIE and RUMFORD? His whole theory is an application of results obtained in the laboratory.†

What I have stated regarding WILSON applies also to SIX, who concluded from his experiments "that the greatest differences at night in point of temperature, between bodies on the surface of the earth and the atmosphere near it, are those which take place in very cold weather." This is quoted from WELLS,‡ who, in his Essay on Dew, recurs more than once to the subject. He signalises, but does not explain, "the greater difference which takes place in very cold weather, if it be calm and clear, between the temperatures of the air and of bodies on the earth at night, than in equally calm and clear weather in summer."§ A considerable number of observations bearing upon this point are scattered through the Essay. The radiant power of the air being practically *nil*, it retains for a considerable time the warmth imparted to it during the day, while when it is dry, the rays from the surface of the earth pass unimpeded through it. Hence the relative refrigeration of the surface.||

In regard to the action of water vapour MAGNUS considered experiment superfluous, as the phenomenon of dew sufficed to prove me wrong. If the vapour possessed the power which I ascribed to it, he contended that dew could not be formed. It is not difficult to dispose of this objection. The formation of dew and superficial refrigeration are connected, not by coincidence but by opposition. I would venture to predict that where the one is great the other, in general, will be small. "Very little dew," says

\* Mr. HILL, the Meteorological Reporter for the North-Western Provinces of India, writes thus:—"There is even, on the part of some, an evident reluctance to accept the decision of laboratory experiments on the question of atmospheric absorption as final, however ingenious, varied, and consistent with one another the experiments may be."—Proc. Roy. Soc., vol. 33, p. 216.

† "Its complete theory," says WELLS, "could not possibly, in my opinion, have been attained, before the discoveries on heat were made, which are contained in the works of Mr. LESLIE and Count RUMFORD."—Essays, p. 191.

‡ Essays, p. 176. WELLS thus generously refers to the labours of WILSON. "Indeed, several of my experiments upon dew were only imitations of some which had been previously made on hoar frost, by that ingenious and worthy man."—Essays, p. 151.

§ Ibid., p. 188.

|| It ought to be stated that, contrary to SIX and to WELLS, Mr. GLAISHER has found that "the differences between the temperature of the air and of bodies on the earth at night, in equally clear and calm weather, were the same at every period of the year." (Phil. Trans., 1847, p. 126.) He moreover records differences considerably in excess of those observed by WILSON and by WELLS. Keeping the action of aqueous vapour in view, the elaborate paper of Mr. GLAISHER might repay further discussion.

WELLS, "appeared on the two nights of the greatest cold I have ever observed on the surface of the earth, relatively to the temperature of the air, both of them having occurred after a long tract of dry weather."\* This evidence is specially valuable in view of the fact that WELLS knew nothing of the action of water vapour on radiant heat. On another occasion he observed a difference of  $9\frac{1}{2}$  degrees between the temperature of the air and that of wool placed upon the earth, without any deposition of dew whatever upon the chilled wool.† He supplements these observations by one equally important in the opposite direction. "On the night," he writes, "which afforded the most copious dew ever observed by me, the cold possessed by the grass beyond that of the air was for the most part only  $3^{\circ}$  and  $4^{\circ}$ ."‡ The smallness of the refrigeration in this instance, and the copiousness of the dew, I refer to one and the same cause; namely, the abundance of vapour. Heavy dew implies this abundance; abundant vapour, if not too local, implies checked radiation, and checked radiation tends to abolish the difference of temperature between air and soil.

WELLS had a theory of his own to account for the association of moderate refrigeration and heavy dew. The heat rendered free by the condensation of the vapour to liquid "prevented" the cold. He tried to determine the effect of condensation by the following experiment.§ To 10 grains of wool he added 21 grains of water, this being the quantity of dew deposited on wool in one of his observations. He placed the moistened wool in a saucer on a feather bed in a room, and determined the chill produced by its evaporation. After eight hours, while the wool still retained  $2\frac{1}{2}$  grains of moisture, its temperature was  $4^{\circ}$  lower than that of a dry saucer placed near it on the same feather bed. When the process is reversed, condensation instead of evaporation coming into play, the foregoing amount of heat, WELLS contended, would be liberated on the grass, and thus prevent inordinate refrigeration.

In thus reasoning WELLS went to the limit of the knowledge of his time, and the explanation here given is a philosophical one. But I do not think it a sufficient explanation. The grass is exposed to the open atmosphere, and the heat developed by every successive film of moisture condensed upon its blades, is instantly wasted by radiation. Those who are accustomed to work with the thermopile know how rapidly the associated galvanometer needle falls from a high deflection to zero, when the heat incident upon the pile is suddenly cut off. A similar rapidity of waste would assuredly occur during the slow formation of dew. The heat of condensation could not for this

\* Essays, p. 186.

† Ibid., p. 183. WELLS sometimes found wetted wool to lose weight, while dry wool gained no weight though lowered many degrees below the temperature of the air, p. 184.

‡ Ibid., p. 169. From a remark occurring at page 135, it may be inferred that the night here referred to was that common to the 29th and 30th of July, 1813. On the two occasions first mentioned, when there was but little dew, the grass was in one instance  $12^{\circ}$ , and in the other  $14^{\circ}$  colder than the air.

§ Essays, p. 187.



reason be housed in the manner supposed by WELLS.\* The true explanation I hold to be that already indicated—the checking of radiation by vapour, the abundance of which was indicated by the copious deposition of dew.

If the experiments of WILSON could be made in an atmosphere still colder than that in which he worked,—on a large plain, for instance, and in a country remarkable for the dryness of its air—WELLS considered that a difference of at least  $30^{\circ}$  would be observed on serene nights between the air and a downy substance placed on the earth. And as SIX had found the air temperature at an elevation of 220 feet to be  $10^{\circ}$  higher than at 7 feet, these  $10^{\circ}$  being added to the  $30^{\circ}$  would make the surface at least  $40^{\circ}$  colder than the air at the height of 200 or 300 feet. With all this I agree. I would go even further, and reiterate here a statement made by me nineteen years ago, that the withdrawal of the aqueous vapour of our atmosphere, for a single calm night, would kill every plant in England capable of being killed by a freezing temperature.

PICTET, I believe, was the first to notice that the temperature of the air near the earth's surface on serene nights diminished as the surface was approached, the sequence of the day temperatures being thus inverted. To account for the chilling of the air say at 10 feet above the earth's surface beyond that at 100 feet above the surface, WELLS invoked the radiant power of the air itself. It is chilled, he thought, by its own emission against the cold earth underneath. WELLS takes great pains to prove that the air possesses this power; and if not the air, the floating matter of the air will, he contends, exert the necessary radiation. Difficulties of this nature not unfrequently crop up in works on meteorology, but they disappear in presence of the fact, that mixed with the air is a gaseous constituent, small in quantity, but capable of producing the effects needing explanation.

As an example of such difficulties, I have already referred to Sir JOHN LESLIE's paper "On certain impressions of cold transmitted from the Higher Atmosphere."†

\* WELLS himself observed in grass a fall of temperature of  $7^{\circ}$  in twenty minutes. This gives us some notion of the rapidity with which a radiant so powerful as water would dispose of its heat.—*Essays*, p. 157.

At the instance of my friend Mr. FRANCIS GALTON, and with the kind sanction of the Meteorological Council, the following instructive observations, showing the temperatures recorded by two thermometers, the one placed on cotton-wool resting on the earth, and the other hung at a height of four feet in the air, were recently made by Mr. WHIPPLE at Kew:—

Time.	Air.	Wool.
4.20 P.M. . . . .	$34.8^{\circ}$ . . . .	$33.2^{\circ}$
„ 25 „ . . . . .	$32.5$ . . . .	$27.6$
„ 30 „ . . . . .	$32.4$ . . . .	$25.7$
„ 35 „ . . . . .	$32.4$ . . . .	$23.4$
„ 40 „ . . . . .	$32.2$ . . . .	$21.7$
„ 45 „ . . . . .	$32.2$ . . . .	$20.7$

The rapidity of radiation is well shown by these observations, an exposure of twenty-five minutes sufficing to establish a difference of  $11.5^{\circ}$ .

† Transactions Roy. Soc. of Edinburgh, vol. viii., p. 483.

He there describes the *Æthrioscope*, an instrument used to measure these impressions. "The sensibility," he says, "of the instrument is very striking, for the liquor incessantly falls and rises in the stem with every passing cloud. Under a fine blue sky, it will sometimes indicate a cold of 50 millesimal degrees; yet on the other days, when the air seems equally bright, the effect is only 30°. The causes of these variations are not quite ascertained." He might have said, not at all ascertained. The causes, I submit, are the variations of the quantity of transparent aqueous vapour in the atmosphere, which, without affecting the visual brightness of the air, is competent to arrest radiation from the earth. Precisely of the same character is the difficulty noticed by Lieutenant HENNESSEY in his paper on "Actinometrical Observations in India." Like LESLIE he speaks of variations, the causes of which are not ascertained. "Again," he says, "there is a change of intensity from day to day apparently not due to alterations in the sun's declination, so that the average daily curve (about noon) is higher or lower without any visible reason."\* The reason here is that applicable in LESLIE's case; namely, the variations of the invisible atmospheric vapour.

In 1866 my friend Professor SORET of Geneva favoured me with a letter from which the following is an extract:—"In two comparative experiments, made within a few days at Geneva and Bologna, the most powerful radiation was obtained at Geneva, although at Bologna the heavens were visibly *purer*. The result appears to me to support your views regarding the aqueous vapour of the air; for the tension of aqueous vapour at Bologna was 10·7 while at Geneva it was only 6·33."

Cautiously abstaining from drawing a general conclusion from a single fact, M. SORET, in 1868, made some further experiments on solar radiation. The intensity was measured by first allowing the rays to fall directly on the thermometer of the actinometer, and then by allowing them, prior to meeting the thermometer, to pass through 5 centimeters of water. Calling the first temperature  $T$  and the second  $t$  the ratio  $\frac{t}{T}$  will be obviously greatest when the absorption by the water is least. And as we know that water exerts its chief absorbent power on the ultra-red rays of the spectrum, the variations in this ratio observed at different atmospheric thicknesses will enable us to infer the nature of the heat "arrested" by the atmosphere.

M. SORET found the ratio to be greater in the middle of the day than when the sun is near the horizon. At 12.30, for example, on the 9th of March the ratio was 0·594, while at 5.10, on the same day, it was only 0·409. A smaller fraction of the total heat was absorbed by the water near mid-day than near sunset. At mid-day therefore the solar heat was more thoroughly sifted of its calorific rays, and more transmissible by water, than it was when the atmospheric thickness was much greater. It would seem difficult to reconcile this result with the notion that aqueous vapour is the absorbing constituent of the atmosphere.

A year subsequently MM. DESAINS and BRANLEY found, both at Paris and at

\* Proc. Roy. Soc., vol. xix., p. 228.

Lucerne, that the sun's heat was always more transmissible through water and alum in the morning than at mid-day. I have too much confidence in the able experimenters here named to think any of them wrong. How then is the discrepancy between them to be accounted for? I think in the following way. What is called the glow of the Alps varies greatly with the quantity of suspended matter in the air. When pronounced, it shows that the more refrangible constituents have been in great part removed from the sun's rays. The proportion of the less refrangible rays in the total radiation is augmented in this way, the relative transmissibility of the heat being diminished. It was, I would suggest, heat that had its character impressed upon it in this way by scattering, and not by absorption, that yielded the result obtained by M. SORET.

Whatever may be the value of this explanation, one result of great interest to me was established by the two French experimenters. Simultaneous observations were made by them on the summit of the Rigi and at Lucerne, the vertical distance between both stations being 4,756 feet. Within this stratum 17·1 per cent. of the solar rays was absorbed.

Experiments were made at the same time at both stations on the perviousness of water to the solar rays. If, as I contend, a vapour and its liquid absorb the same rays, the withdrawal of 17 per cent. of the radiation by aqueous vapour must render the residual heat more transmissible by water. This is precisely what the French experimenters found it to be. "Through a glass trough 0·08 of a meter in length, and full of water, the rays on the Rigi passed in the proportion of 685, and at Lucerne in the proportion of 730, per 1,000 of the incident heat."

MAGNUS was so convinced of the impotency of aqueous vapour to arrest radiant heat, that in reference to various meteorological phenomena, where the action I had ascribed to it offered a satisfactory explanation of the facts, he put in its place mist or haze, the existence of which he assumed, even when neither mist nor haze was visible. There are various passages in the Essay on Dew which it would be difficult to reconcile with this assumption; for they show that even visible atmospheric turbidity has by no means the influence which MAGNUS ascribed to it.

Thus on the 7th of January, 1814, WELLS observed "a little after sunset" a refrigeration of  $8^{\circ}$ , at a time when some parts of the sky were covered with clouds, and the lower atmosphere a little obscure.\* On another evening, "when the atmosphere was neither very clear nor very still" a difference of  $14\frac{1}{2}^{\circ}$  was observed between the temperatures of air and swan down. WELLS also observed a refrigeration of  $5^{\circ}$  when the sky was thickly covered with high clouds. A very definite observation in regard to haze was made on the 21st of January, 1814. The air at this time was "a good deal hazy."† Notwithstanding this, the temperature of swansdown placed on snow was  $13\frac{1}{2}^{\circ}$  lower than that of the air 4 feet above it. Thus, if other circumstances be favourable, that is to say, if the air be dry, even a visible haze does not prevent

\* Essays, p. 174.

† Ibid., p. 176.

powerful refrigeration. I close these references to mist and haze by mentioning a most striking observation made by WELLS on the 1st January, 1814. "I found," he says, "during a dense fog, while the weather was very calm, a thermometer lying on grass thickly covered with hoar frost,  $9^{\circ}$  lower than another suspended in the air 4 feet above the former."\* Here, as before, low temperature implies scanty vapour, the absence of which enabled the grass to pour its heat even through the interstices of a dense fog.†

I could draw still further on this admirable Essay in illustration of the thesis which I have so long defended. As a repertory of valuable facts and penetrative arguments it probably stands unrivalled in the literature of meteorology. One point remains which cannot be passed over. It has reference to the part played by clouds in arresting and returning the radiation from the earth. "No direct experiments," says WELLS, "can be made to ascertain the manner in which clouds prevent, or occasion to be small, the appearance of a cold at night, upon the surface of the earth, greater than that of the atmosphere; but it may, I think, be firmly (fairly?) concluded from what has been said in the preceding article, that they produce this effect, almost entirely, by radiating heat to the earth, in return for that which they intercept in its progress from the earth towards the heavens."‡ WELLS had the strongest analogies to adduce in favour of this view. He placed boards and sheets of paper above his thermometers, thus screening them from the clear sky; and in that beautiful passage where he speaks of "the pride of self knowledge," and refers to the simple devices which experience had taught gardeners to apply for the safety of their plants, he mentions the protection which even a thin cambric handkerchief can afford to thermometers over which it is spread. He was irresistibly led to conclude that clouds acted in the same fashion, and that when they occupied the firmament, they sent back to the earth the heat incident upon them, exactly as the board, and the paper, and the cambric, sent it back in experiments made close to the surface of the earth.

But in the enunciation of this hypothesis his knowledge and penetration as an observer came, as usual, into play. He is careful to distinguish between high clouds and low clouds. "Dense clouds," he says, "near the earth," must possess the heat of the lower atmosphere, and will therefore send to the earth as much, or nearly as much, heat as they receive from it by radiation. But similarly dense clouds, if very high, though they equally intercept the communication of the earth with the sky, yet being from this elevated situation colder than the earth, will radiate to it less heat than they receive from it, and may consequently admit of bodies on its surface becoming several degrees colder than the air."§

\* Ibid., p. 158.

† Mr. GLAISHER moreover has found differences of from  $10^{\circ}$  to  $12^{\circ}$  between grass and air "at times when the sky has been free from clouds but not bright, haze and vapour being prevalent." (Phil. Trans., 1847, p. 145.)

‡ Essays, p. 205.

§ Ibid., p. 206. "If," says WELLS, in another place, "the clouds were high and the weather calm, I

MAGNUS urged this point against me, and I may be permitted to say that I always considered it one of his strongest points; my holding of this opinion being however dependent on the views which I entertained, and which were opposed to those of MAGNUS, regarding the relation of liquid to vapour. If, as I believe, the absorbent power is not enhanced by condensation—if in this respect water behaves like hydride of amyl and sulphuric ether—then I do not think that such a process of reverberation, between earth and clouds, as that assumed by WELLS is possible. The aqueous vapour in a very few thousand feet of air, of average humidity, would, if condensed, form a layer of water 0·5 of an inch in thickness, and through such a layer, or even through a thinner layer, the earth's radiation could not pass. If the earth's radiation reach the clouds it must be by a process similar to that of handing buckets from man to man in the case of a fire. The heat must be taken up and re-radiated, we know not how many times, before the clouds are reached. I do not, however, think this mechanism of discharge necessary. Low clouds will not form above exposed thermometers, in weather previously serene, unless some change has occurred in the atmosphere; and change may occur where no cloud reveals it. It may extend, and in most cases probably does extend, from the low clouds to the earth. I think it in the highest degree probable that in most, if not in all the cases cited by WELLS, of thermometers rising when clouds were formed overhead, the precipitation was due to the intrusion of humid air, the humidity extending invisibly from the clouds downwards. To this, I believe, rather than to any immediate exchange of temperature with the clouds, the rapid and considerable changes of temperature referred to by him at pp. 156 and 157 of the Essay are to be ascribed. Future observations will, doubtless, bring this view to an experimental test.

I here recur with renewed pleasure, to a paper published by General STRACHEY in the Philosophical Magazine for July, 1866. It was probably intended as a reply to the strictures of MAGNUS; and to me it appears cogent in the highest degree. General STRACHEY calculated the fall of temperature from 6<sup>h</sup> 40<sup>m</sup> P.M., Madras time, to 5<sup>h</sup> 40<sup>m</sup> next morning, for a certain number of days, selected as sufficiently clear. He also calculated the mean vapour tension during the nights, and tabulated the results according to the quantity of vapour for the years 1841, 1842, 1843 and 1844. In such observations, as pointed out by STRACHEY, discrepancies are to be expected, but the general result is unmistakable, that the fall of temperature by radiation is greatest when the air is driest, and least when the air is most humid. A series of observations made at Madras between the 4th and the 25th of March, 1850, are particularly suitable for the illustration of this law of action. During the period referred to "the sky remained remarkably clear, while great variations of the quantity of vapour took place." Here are the results as tabulated by General STRACHEY:—

have sometimes seen on grass, though the sky was entirely hidden, no very inconsiderable quantity of dew."—*Ibid.*, p. 128.

Tension of vapour.	·888.	·849.	·805.	·749.	·708.	·659.	·605.	·554.	·435.
Fall of temperature from } 6 <sup>h</sup> 40 <sup>m</sup> P.M. to 5 <sup>h</sup> 40 <sup>m</sup> A.M. }	6°0	7°1	8°3	8°5	10°3	12°6	12°1	13°1	16°5

These results, if correct, and I am not aware that they have ever been questioned, show in the most impressive manner the influence of the aqueous vapour of our atmosphere on our planet's radiation. As the vapour diminishes, the door opens, which permits the escape of the earth's heat. The halving of the vapour tension nearly trebles the refrigeration of the thermometer.

Equally clear is the evidence given by General STRACHEY as to the action of aqueous vapour upon the radiation of the sun. Here are the results :—

Tension of vapour.	·824.	·737.	·670.	·576.	·511.	·394.
Rise of temperature from 5 <sup>h</sup> 40 <sup>m</sup> A.M. } to 1 <sup>h</sup> 40 <sup>m</sup> P.M. .. .. . }	12°4	15°1	19°3	22°2	24°3	27°0

This table is the exact complement of the last. *There* the *fall* of temperature was powerfully promoted by the withdrawal of the vapour. *Here* the *rise* of temperature is powerfully promoted by the same cause.\*

But the most impressive illustration of the action of aqueous vapour is now to be referred to. In 1865 I subjected to examination the radiation from the electric light produced by a battery of 50 of GROVE's cells, and found, by prismatic analysis, the invisible calorific radiation to be 7·7 times the visible. The determination was afterwards made by the method of filtration, whereby the one class of rays was detached with great sharpness from the other, and both of them rendered measurable. By this method the invisible radiation was found to be 8 times the visible. A close agreement was therefore established between the results of the two methods. Computed from the diagram of MÜLLER the invisible radiation of the sun is twice the visible. This smaller ratio might, of course, be referred to the original quality of the solar

\* Mr. HILL, Meteorological Reporter for the North-West Provinces of India, in a paper recently presented to the Royal Society describes an attempt to determine the "Constituent of the Atmosphere which absorbs Radiant Heat." He uses for this purpose the careful observations made by Messrs. J. B. N. HENNESSEY and W. H. COLE, at Mussoree and Dehra respectively. From the absence of symmetry in the quantities of heat received by the actinometer on both sides of noon at Mussoree, and from the existence of this symmetry at Dehra, he infers the periodic lifting and lowering of the absorbing constituent above and below the higher station. He finds the variation of the absorption coefficient to follow the variations of vapour tension. From this and from a similar result obtained by a second method of calculation, he draws the conclusion "that there can be very little error in agreeing with Dr. TYNDALL that the absorptive power of dry air is sensibly nothing, and that the total absorptive power of the atmosphere is due to the water vapour it contains." A most interesting discourse on Solar Heat, by M. VIOLLE, of Grenoble, will be found in the *Revue Scientifique* for 1878, p. 944. I guard myself against saying that the diathermancy of dry air is *perfect*.

emission, the ratio holding good up to the surface of the sun. But having placed, as I thought beyond doubt, the action of aqueous vapour on radiant-heat, and believing the action of the vapour to be substantially the same as that of water, I reasoned and experimented as follows in 1865 :—"The sun's rays, before reaching our earth, have to pass through the atmosphere, where they encounter the atmospheric vapour which exercises a powerful absorption on the invisible calorific rays. From this, apart from other considerations, it would follow that the ratio of the invisible to the visible radiation in the case of the sun must be less than in the case of the electric light. Experiment, we see, justifies this conclusion. If we cause the beam from the electric lamp to pass through a layer of water of suitable thickness, we place its radiation in approximately the same condition as that of the sun; and on decomposing the beam, after it has been thus sifted, we obtain a distribution of heat closely resembling that observed in the solar spectrum."

If therefore, we could get above the vapour-screen which swathes the earth, the "powerful absorption" referred to in the paragraph just quoted would disappear, the ratio of the invisible to the visible solar rays being augmented correspondingly. That such would be the case I have long taken for granted, but I hardly hoped for a corroboration so impressive as that furnished by the recent observations of Professor LANGLEY, in the Sierra Nevada Mountains of California. Professor LANGLEY is known to have highly distinguished himself by researches on radiant heat, with instruments of his own invention—he writes to me thus from Mount Whitney, California, Sept. 10, 1881 :—

"I received your letter just as I was starting on the expedition to this point of which I wrote. I much regretted that I had not time to provide myself with your mercury pyrheliometer, so I have been obliged to use the old form, with its many disadvantages.

"Our route here has led us through the driest parts of this continent, and across rainless deserts to this mountain, where the air is perhaps drier than at any other equal altitude ever used for scientific investigation. I write from an altitude of 12,000 feet, while the 'Peak' rises nearly 3,000 more above me. I have been successful in bringing up, and using here, the rather complex and delicate apparatus for investigating the absorption of the atmosphere on homogeneous rays, throughout the visible and invisible spectrum.

"You may be interested in knowing that the result indicates a great difference in the *distribution* of the solar energy here from that to which we are accustomed in regions of ordinary humidity; and that while the evidence of the effect of water vapour on the more refrangible rays is feeble, there is, on the other hand, a systematic effect due to its absence which shows by contrast its power on the red and ultra-red in a striking light.

"These experiments also indicate an enormous extension of the ultra-red spectrum

beyond the point to which it has been followed below ; and being made on a scale different from that of the laboratory—on one indeed as grand as nature can furnish—and by means wholly independent of those usually applied to the research, must, I think, when published, put an end to every doubt as to the accuracy of the statements so long since made by you, as to the absorbent power of this agent over the greater part of the spectrum, and as to its predominant importance in modifying to us the solar energy.

“ I am, with much regard,

“ Very truly yours,

“ S. P. LANGLEY.”